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METHODS IN CHEMICAL ANALYSES OF SOILS

This number of SOIL SCIENCE is devoted exclusively to papers concerned with techniques involved in chemical analyses of soils. The contributors were chosen by a committee serving at the request of the editor, who hereby acknowledges with appreciation the help of the committee.

It is apparent that many capable soil chemists are not included among the contributors to this special issue, and it is possible that some soil chemists may be in fundamental disagreement with one or another of the techniques presented in these papers. If so, it is hoped that those who have improvements to suggest will discuss them with the authors so that when the time arrives for a revised edition all such suggestions may have been given adequate consideration.

It must be kept in mind that these methods are in no wise "official." They are merely what the authors consider good for average requirements, involving both simplicity and reliability. In most instances, methods requiring expensive special apparatus, even though they might be much speedier for mass output from the laboratory and equally accurate, have not been presented.

The editor wishes to express his appreciation for the time given by the contributors to this special issue of the Journal and the careful manner in which the papers have been prepared. It is believed that many soil chemists will find themselves greatly indebted to these men for having joined in this undertaking.

FIRMAN E. BEAR

METHODS OF COLLECTING AND PREPARING SOIL SAMPLES

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An earlier paper discusses the principles upon which the methods presented here are based.² These methods must be modified to satisfy the particular objective of each sampling problem, but any method used should meet the restrictions imposed by statistical principles, upon which sound sampling procedure depends.

DEFINITIONS

A *sampling unit*, as used in this paper, is a single core or slice of soil taken by a sampling tool. One or more sampling units that, collectively, represent a given soil volume constitute a *sample*. Each soil volume to be represented by a sample may be considered a *sampling volume*; its horizontal exposure, a *sampling area*. The point within a sampling area at which a sampling unit is taken is a *sampling site*. Each sampling unit may be treated as a statistical *individual*; the aggregate of all possible sampling units in a sampling volume, as a statistical *population*.

SAMPLING TOOLS

A sampling tool should provide an uncontaminated sampling unit of uniform cross section throughout the thickness of the horizon sampled. For compositing, the dimensions of the sampling unit taken should be reproducible. Several kinds of blades, tubes, and augers meet these requirements if properly used. Sampling tubes, which cut a core of uniform cross section as they are forced into the soil, are efficient in nonstony, moist, medium-textured soils if supplementary observations of the undisturbed soil are not required. They are especially efficient in such soils for drawing sampling units of the upper horizons for compositing. A 16-inch tiling spade with a round point is better suited to dry, stony, or heavy-textured soils. Twenty circular holes 18 inches across and 16 inches deep can be dug, and a 3- or 4-inch slice can be cut from the wall of each with the spade, laid on the surface, and sampled with a trowel in an hour. Tapered post-hole augers take sampling units biased with depth, contaminate subsoil samples with material from overlying horizons, and destroy soil structure. A parallel-sided, completely sheathed auger that operates on the same principle is efficient for dry sandy soils. The ordinary wood-bit or screw auger takes sampling units that are not uniform with depth and not reproducible, contaminates subsoil samples with overlying material, and destroys soil structure.

SAMPLES TO REPRESENT A SPECIFIED AREA

Examine the soil of the area with a spade or auger to detect horizontal variations and distinguishable horizons, observe subareas that support abnormal plant growth, and obtain

¹ Assistant professor of soil science, department of agronomy.

² Cline, M. G. 1944 Principles of soil sampling. *Soil Sci.* 58: 275-288.

information on past treatment. On the basis of this information, subdivide the tract into separate sampling areas, each of which is uniform with respect to soil type, land use, recent applications of fertilizer and lime, and plant growth. Subdivide large, apparently uniform areas arbitrarily into the smallest sampling areas significant for the objective and/or feasible to sample as a unit. On experimental fields the minimum feasible sampling area may be an experiment, a block, or a plot; for a "soil-testing service" it should be the minimum area a farmer can be expected to treat as a unit. If the smallest feasible sampling area contains two or more distinctly different soil conditions, either sample each separately or sample only the one that will control the farmer's practices for the area as a whole.

Within each sampling area choose as sampling volumes the horizons or parts of horizons that will satisfy the objective; do not sample by arbitrary depths except within horizons. For fertility diagnosis, sample separately the topmost 6 inches of the plowed layer and a 6-inch layer of a subsoil horizon penetrated by plant roots. Sample the topmost 2 inches of pastured soils separately from the remainder of the upper horizon.

If the range or variance of sampling units can be approximated, determine the number of sampling units required to give a reliable estimate of the mean of each sampling volume by the method described by Cline.³ Preliminary studies by rapid chemical methods are often justified to approximate these statistics for projects that involve detailed analytical procedures. If no estimate can be made, the number of sampling units must be decided arbitrarily. Twenty sampling units of the plowed layer, or ten of a subsoil horizon, is commonly a minimum number per sample from cultivated soils not fertilized within the crop year. One hundred or more sampling units per sample may be required from soils that have recently received a broadcast application of the element under test.

A. To establish only estimates of mean values

Locate the required number of sampling sites by pacing predetermined distances along the lines of a grid superimposed on the area at random. To avoid systematic bias, lines of the grid should not parallel known soil variations or the direction of cultural operations. At each sampling site, remove all vegetable matter not incorporated with the soil, and draw a sampling unit from each horizon to be sampled by means of a spade and trowel, a sampling tube, or a completely sheathed parallel-sided post-hole auger. Combine, in clean pails, the sampling units of each horizon as taken, until all sites have been sampled. If the composite sample obtained is larger than is required, pour each composite on a clean piece of oilcloth or canvas; crush all clods to less than $\frac{1}{4}$ -inch pieces; thoroughly mix by rolling; cone; and quarter to the desired size. If less than 1 quart is to be taken, crush all aggregates to less than $\frac{1}{4}$ -inch particles before mixing. Place the sample in a clean cotton bag or cardboard carton, or if moisture is to be determined, in a clean metal container with a tightly fitting cover; label; and transport as quickly as possible to a suitable place for drying.

B. To establish estimates of variability among sampling units

Locate sampling sites and draw sampling units in the manner described under section A, but keep each sampling unit separate for analysis. Two or more composite samples drawn from the same sampling area will provide an estimate of variability among composites. Variance of sampling units may also be calculated from data derived from several replicate composite samples.

C. To establish estimates of significance and fiducial limits

Locate the required number of sampling sites by complete randomization. A systematic scheme, such as a grid, should not be used. A satisfactory method of randomization is to diagram the area in squares, number each square, and draw at random from a series of corresponding numbers until the required sampling units have been located. Complete

³ *Ibid.*

randomization should not be attempted if the number of sampling units is small. Draw the sampling units in the manner described under section A and keep each one separate for analysis, or take two or more similarly drawn composite samples for each of the sampling volumes compared.

SAMPLES TO REPRESENT A SOIL TYPE

Examine the soil profile at several places and select a site representative of the modal profile of the soil type to be studied. Select a virgin soil if possible; never sample in road cuts or old excavations. Dig a rectangular pit deep enough to expose the parent material and large enough to permit easy observation of the entire profile. The pit should be so oriented that one wall is as uniformly lighted as possible. Pick that wall with a knife or trowel to clean the profile and expose natural structure. Delimit recognizable horizons and describe the complete profile, as well as external features of the environment. Divide each thick horizon arbitrarily into 3-inch layers, and sample each layer by removing about a quart of soil with a trowel in "steps" from the surface downward. Place each sample in a labeled cloth bag or cardboard carton and transport to a suitable place for drying. Samples of the deeper-lying parts of the C horizon may be taken with a sampling tube or post-hole auger. To establish type variations, select and sample a number of additional sites at random within areas of the soil type under investigation.

PREPARATION OF THE SAMPLE

As soon as possible after sampling, break up any large clods and spread the sample to air-dry on a clean wooden tray or a strong paper in a clean warm room free from dust and contaminating gasses. If the sample is small, it may dry rapidly enough in the uncovered container in which it was taken. When air-dry, crush the aggregates with a hardwood or rubber-capped pestle in a clean, agate or porcelain mortar without grinding primary particles. Large aggregates may be crushed by rolling with a hardwood rolling pin on a smooth, hard, clean surface. After a short period of crushing, sift the sample through a sieve with holes 2 mm. in diameter and return the coarse material retained to the mortar for further crushing. Repeat until only primary particles and organic residues remain on the sieve. This coarse material may be discarded.

If results of analysis are affected by grinding primary particles, mix the 2-mm. material by rolling on clean paper; cone; quarter, or divide in a riffle sampler, to a size convenient for stock; and store in a closed glass container. For analyses that are not affected by the crushing of primary particles, grind the sample of material passing the 2-mm. sieve in a mechanical grinder to any fineness required. Analytical results should be expressed on the base of all material less than 2 mm. in diameter.

SUMMARY

Methods of sampling soils, first, to represent an area for estimates of mean values only, estimates of variability, and estimates of significance and fiducial limits and, second, to represent a soil type are presented. Instructions for subdivision of areas and selection of sampling sites are included. The relative merits of general types of sampling tools are pointed out. A method of preparation of samples for analysis is given.

THE FUSION ANALYSIS OF SOILS

DETERMINATION OF Si, Ti, Al, Fe, Mn, Ca, Mg, K, Na, and S

W. O. ROBINSON

U. S. Department of Agriculture¹

Data obtained by fusion analyses are useful mainly to the soil scientist rather than to the practical agriculturist. An exception to this generality occurs, however, when minimum quantities of certain elements are indicated in the soil and the analytical method employed is sufficiently sensitive. Fusion analysis gives little evidence as to the manner in which the various elements are combined and indicates very little as to the availability of these elements for plant growth.

The methods employed in the fusion analyses of soil are those previously worked out for and adapted to the analyses of minerals and rocks. A fuller description of the principles involved in the methods which follow are given by Hillebrand and Lundell.² The procedures here described have been selected by the experience of some 25 analysts in this division through a period of more than 30 years and have been found to give reliable results with a wide variety of soils.

Considerable care is necessary to obtain accurate results for such elements as calcium, magnesium, potassium, sodium, and sulfur in some of the very sandy soils of the Coastal Plains. Blanks must be run on the reagent, and in some cases it is doubtful whether these elements are present in estimable quantities.

In agricultural analyses two systems are used for reporting the results; one, the element percentage; and the other, the oxide of the element. In reporting the fusion analyses of soils there is excellent reason for using the oxide form, for then the sum of the percentages should closely approach 100. This is a check on the accuracy of the work. The presence of organic matter, clay minerals of indefinite degrees of hydration, the different degrees of oxidation of iron and perhaps other elements, and the volatilization of some elements make this summation test much less rigorous than in the case of minerals or rocks. Nevertheless, it is a very useful check.

Preparation of sample. Pass the well-mixed air-dry sample through a sieve having circular holes 2 mm. in diameter. Quarter the sieved soil to a minimum of 25 gm., grind in an agate mortar, and pass through 100-mesh bolting cloth.

Moisture determination. The weight of soils varies considerably with the moisture of the air. Consequently a moisture determination must be made on the air-dry sample at the time the sample is weighed out for the major constituents. For this moisture determination, weigh out about 2 gm. of the ground soil in a shallow weighing bottle that can be tightly stoppered. Place the weighing bottle with cover, but uncovered, in a drying oven regulated at 110°C. and keep there overnight. Cover the weighing bottle in the oven, cool in a desiccator $\frac{1}{2}$ hour, and weigh.

¹ Division of Soil and Fertilizer Investigations, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, Beltsville, Maryland.

² Hillebrand, W. F., and Lundell, G. E. F. 1929 Applied Inorganic Analysis. John Wiley and Sons Co., New York.

Loss on ignition. Weigh accurately 0.5–1.0 gm. of the well-mixed and ground soil (depending on the content of iron and aluminum, which cause bulky precipitates) into a 15-ml. platinum crucible. Heat slowly (to avoid mechanical loss) in an electric furnace or over a Bunsen burner to about 700°C. and hold there $\frac{1}{2}$ hour. If a Bunsen burner is used, adjust the cover over the inclined crucible so that the contents have free access to the air. Cool the crucible in a desiccator and weigh. Ignite an additional 15 minutes to check the constancy of weight. In this connection, bear in mind that an ordinary platinum crucible may loose 0.2 or 0.3 mgm. during a half hour's ignition. Reserve the crucible and contents for the determination of the major elements.

The fusion. Mix the residue from the loss-on-ignition determinations with five times its weight of c. p. sodium carbonate. Put a closely fitting cover on the crucible and heat cautiously until the flux has melted and the fusion is quiet. After the fusion is quiet (or bubbling is over) apply the full heat of a good Bunsen burner or the moderate heat of a blast lamp for 10 minutes longer. While the contents are still molten, hold the crucible with the tongs and whirl or turn it until the melt cools on the sides, leaving as little as possible on the bottom. Cool the crucible on a slab of iron or alberene and detach the melt immediately from the cooled crucible by inverting it over a 250-ml. beaker or a large platinum dish and rolling it between the fingers with gentle pressure against the sides. Disintegrate the melt with hot water. This operation will take time. Leave the crucible and cover, to which some of the fusion will adhere, immersed in hot water in the receptacle chosen. After the melt is thoroughly disintegrated, wash it off the crucible and cover into the dish or beaker and add a few drops of ethanol to reduce the green manganate. Otherwise free chlorine, which will be formed by interaction of the manganate and hydrochloric acid, will attack the platinum evaporating dish. If porcelain or glass dishes are used the ethanol is not necessary.

Silica. When the greenish color of the disintegrated melt has disappeared add slowly 15 ml. concentrated HCl to the covered receptacle. Evaporate to dryness on the steam bath. It is well to continue this heating overnight so that the separated silica gel may be sufficiently dehydrated. Take up the residue with 15 ml. concentrated HCl and 15 ml. hot H₂O, filter, and wash with hot water until practically free from chlorides. Again evaporate the filtrate to dryness to precipitate any silica not retained in the first precipitate, take up with 15 ml. concentrated HCl and hot water, filter, and wash free from chlorides into a 250-ml. beaker. Combine the two precipitates and ignite the mixture, preferably in the crucible in which the fusion was made. Ignite slowly at first to avoid mechanical loss, a common source of error in silica determinations. The light, feathery silica is easily blown by air currents. After the carbon has been thoroughly burned from the precipitate, ignite at the full temperature of the blast lamp from 20 minutes to half an hour.³ Check with 10-minute period of blasting to constant weight, bearing in mind that the crucible itself may loose 0.1 to 0.2 mgm. during this period. After the weight has become constant, moisten the silica with water, add 6–8 ml. strong HF, a few drops dilute H₂SO₄, and evaporate cautiously to dryness. If the residue is more than 3 or 4 mgm.⁴ treat again with a little HF as before. Ignite the crucible for a minute or so over the blast lamp, cool, and weigh. Save the crucible and contents for the ignition of the iron group.

Iron oxide, alumina, and titania. Neutralize the filtrate from the silica determination with a pure ammonia solution using the precipitate as an indicator. Make only very slightly acid with hydrochloric acid and heat to boiling. Precipitate the group with a slight excess of ammonia; an excess of 1 to 2 ml. strong ammonia diluted with its volume of water is sufficient. Boil for 1 minute, allow to settle, and filter when hot into a 400-ml. beaker. Wash the precipitate only slightly, as this is but the first precipitation. Transfer the filter paper

³ This blasting is necessary; no matter how carefully the precipitate is washed, 1–3 mgm. NaCl will be given off in the first stages of the blasting. See Hillebrand and Lundell, p. 545.

⁴ When this quantity is exceeded, barium sulfate is commonly indicated. Sometimes the residue may contain tin, zirconium, columbium, and tantalum.

with its contents to the beaker in which the precipitation was made and dissolve in 10 ml. concentrated HCl and hot water. Macerate the filter paper with two glass rods and add enough water to make the volume to 150 ml. Precipitate the iron group as before, filter and wash thoroughly with hot water containing about 1 per cent ammonium nitrate in the later washings, until the washings are practically free from chlorides. Transfer the filter paper and precipitate to the crucible used for the silica determination, dry, and ignite in the inclined crucible with cover so adjusted as to allow free access of air. Ignite over a blast lamp for 15 minutes or to constant weight.

Transfer the bulk of the ignited iron group precipitate to a 30–40 ml. Pt crucible, add 5–7 gm. $K_2S_2O_7$, and heat very cautiously⁵ over the low flame of a Bunsen burner, keeping the crucible covered. Fuse a small quantity of the $K_2S_2O_7$ in the smaller crucible in which the ignition was made until the contents not transferred to the larger crucible are dissolved. Transfer the contents of the smaller crucible to the larger crucible and fuse until all the solid matter is dissolved. If any undissolved matter adheres to the sides of the crucible after bubbling has receded, bring it again into the melt by manipulation with tongs and flame. After fusion is complete, cool the melt as in the sodium carbonate fusion, add 4 ml. concentrated H_2SO_4 , and dissolve in water, keeping the volume under 150 ml.

Reduction and titration of the iron. Pass H_2S into the solution of the iron group just obtained to reduce the iron and to precipitate dissolved platinum. Boil a few minutes to coagulate sulfur, and filter into a 300-ml. iron reduction flask. Make the volume up to about 200 ml. and pass H_2S through the cold solution at first, then bring slowly to a boil while the H_2S is still passing. Cool about 10 minutes without interrupting the H_2S stream. Then disconnect the H_2S tube and boil off the H_2S , passing CO_2 through the solution meanwhile. Test for complete expulsion of H_2S by means of a filter paper moistened with lead acetate and hold against the opening of the outlet tube. When the H_2S is completely expelled, cool without interrupting the stream of CO_2 and titrate with standard permanganate. If unfamiliar with the process, reduce the iron and repeat the titration. If preferred, the iron may be reduced by SO_2 .

Titanium. Evaporate the liquid from the iron titration to 50 to 75 ml., add 10 ml. concentrated H_2SO_4 and a few drops strong H_2O_2 (free from F), make up to 100 ml. in a measuring flask, and compare in a colorimeter with a standard titanium solution prepared the same way.

Aluminum. From the total weight of the ignited oxides, subtract the sum of the Fe_2O_3 , and P_2O_5 . This difference is Al_2O_3 . Some twenty other elements are included in this "alumina by difference" but ordinarily the quantities of these other elements are so very small that the error is of no significance.

Precipitation of the ammonium sulfate group. Evaporate the combined filtrates from the iron group, preferably in a platinum dish, to slightly less than 100 ml., transfer to a wide-mouthed Erlenmeyer or assay flask, add 2–3 ml. strong ammonia, pass in H_2S to saturation, add 2–3 ml. strong ammonia, then stopper, and let stand overnight. Manganese, zinc, copper, cobalt, and nickel are precipitated as sulfides. Filter and wash with ammonia and ammonium sulfide solution, keeping the funnel covered and washing continuously to prevent oxidization and resolution of the manganous sulfide.

Calcium. Heat the filtrate from the ammonium sulfide precipitation, which should not exceed 150 ml. in volume. Add an excess of recently dissolved ammonium oxalate and digest several hours on the steam bath. Cool and filter through the most retentive filter paper. Ignite the precipitate to render the coprecipitated platinum insoluble, dissolve in dilute HCl, reprecipitate as oxalate, filter, ignite blast, and weigh. Save the combined filtrates for the magnesium determination. If the manganese is not previously removed by ammonium sulfide, some will contaminate the calcium precipitate as revealed by a brown

⁵ The solution is likely to froth and boil over, and in addition there is considerable mechanical loss by spattering, unless the operation is carefully performed.

color. If present it should be determined colorimetrically, and suitable corrections made.

Magnesium. The combined filtrates from the calcium determination should not exceed 175 ml. If necessary, evaporate to this volume. To the cool filtrates add an excess of a solution of sodium hydrogen phosphate slowly and with constant stirring. Add enough ammonia to make the solution about 5 per cent NH_4OH and let stand overnight in a cool place. Filter and wash the precipitate with 2.5 per cent NH_4OH . Dissolve the precipitate in dilute HCl , add only a slight excess of the orthophosphate solution (no more than 2 ml. of a 10 per cent solution) and slowly add ammonia with constant stirring until the precipitate commences to form, add enough strong ammonia to make the solution about 5 per cent NH_4OH . Let stand 2 or more hours and filter and wash with 2.5 per cent NH_4OH until free from chlorides. Dry the precipitate and ignite slowly. The full heat of a good Bunsen burner will ordinarily serve to burn the precipitate white, but occasionally a weak blast lamp is necessary. It is a mistake to blast the precipitate until it fuses to the wall of the crucible.

Calcium is always present in the magnesium precipitate. The quantity present should be determined and suitable corrections applied, especially on the analysis of soils low in calcium. To do this, dissolve the magnesium pyrophosphate in a little warm dilute sulfuric acid, add enough absolute alcohol to make the solution 90 per cent alcohol, cover, and let stand 3-4 hours. Filter and wash with alcohol. Dissolve the calcium sulfate in hot acidulated water, precipitate as calcium oxalate, ignite, and weigh. It is the general experience that, if the procedure has been uniform in all cases, the quantity of calcium found in the magnesium precipitate will be so uniform for a series of analyses that an average correction can be applied in the later analyses without making the actual separation. If no calcium oxalate precipitate is obtained in the calcium determination, probably not enough calcium is present to saturate the solution, and in such cases the quantity of calcium that may be present must be separated from the magnesium precipitate. Manganese should not contaminate the magnesium precipitate, if the separating by ammonium sulfide has been carefully done. If the ammonium sulfide separation has not been used, a separate determination for manganese in the magnesium pyrophosphate must be made and suitable corrections applied.

Manganese. Weigh into a platinum dish 1 or 2 gm. of the soil ground to pass a 100-mesh sieve, and ignite to destroy the organic matter and facilitate decomposition. Treat the ignited residue with 20 ml. HF and 3-7 ml. H_2SO_4 and let stand overnight. Evaporate to dryness on the steam bath. Heat cautiously to the fuming point of the H_2SO_4 , cool, dilute with water. Then repeat the evaporating and fuming. Take up with water and a few drops of sulfurous acid to dissolve any manganese dioxide that may have been formed. Transfer to a 100-ml. measuring flask, make up to volume, mix, and allow to settle.

To an aliquot corresponding to 0.5 or 1.5 gm. soil in a 150-cc. beaker add 20 ml. HNO_3 , 10 ml. H_2SO_4 , and 0.2 to 0.4 gm. potassium periodate. Boil for a minute or so and keep hot for 5-10 minutes while the color is developing. Cool, transfer to a suitable volumetric flask, and compare, in a short-tube colorimeter, with a standard solution of manganese of nearly the same depth of color treated as above.

Potassium and sodium. The well-known J. Lawrence Smith method is the standard for determining the alkalis in minerals. In this method eight times as much flux as soil is used. The calcium carbonate used should not contain more than 0.02 per cent of combined potash and soda.

Weigh out 0.5 gm. of the soil and grind and mix intimately with 0.5 gm. NH_4Cl and 4 gm. CaCO_3 in an agate mortar. Place a small quantity of CaCO_3 in the bottom of a J. Lawrence Smith crucible and transfer the sample and flux to the crucible. Rinse out the mortar with a small quantity of CaCO_3 . Place the covered crucible through a hole in the side of a baked clay or alundum cylinder in such a position that the covered end extends about $\frac{1}{2}$ inch beyond the outside wall. Turning the crucible in the earlier stages of the ignition will facilitate the detaching of the sintered cake. Ignite very slowly at first until the crucible

ceases to smell of ammonia, then apply the full heat of one or two good Bunsen burners to the lower end of the crucible for $\frac{1}{2}$ hour.

Transfer the sintered cake to a 250-ml. beaker and slake with a little water, wash out crucible and cover into the beaker, and leach on the filter until the volume of the wash water is somewhat under 200 ml. Precipitate the calcium as carbonate with ammonium carbonate and ammonia. Filter, wash the CaCO_3 once or twice by decantation, then dissolve in a minimum quantity of HCl , and reprecipitate the CaCO_3 . Filter, wash, and evaporate the combined filtrates in a platinum dish and expel ammonium salts at a temperature just below dull redness ($525^\circ\text{C}.$).

Take up the residue with hot water; precipitate, with a few drops of ammonium oxalate, the small quantity of calcium that may be present; and filter into a small platinum dish. Evaporate to dryness and expel ammonium salts as before. When the residue has burned white, moisten with a few drops of dilute HCl , evaporate, ignite as before for a few minutes, cool, and weigh. Take up with water, pass through a small filter into a porcelain or glass evaporating dish, and wash. Place the filter in the small evaporating dish, ignite, and weigh. The difference in weight gives the weight of the potassium and sodium chlorides. Determine the potassium by precipitation with enough platinic chloride to react with the quantity of chlorides present calculated as KCl . Evaporate to pastiness. Take up with 80 per cent ethanol, collect on a Gooch crucible, dry at 110° , and weigh. Obtain the sodium by difference or, if desired, determine it directly as the zinc-uranyl acetate salt. It is essential to run blanks on the reagents used, including evaporations, as in regular determinations, if evaporations are not made in platinum.

Sulfur. Fuse from 1 to 2 gm. of the finely ground and well-mixed soil in a 15-ml. platinum crucible with five times the weight of Na_2CO_3 and 0.2 or 0.3 gm. NaNO_3 . The fusion is best done in an electric furnace. If gas is used for the ignition, the melt is likely to be contaminated with sulfate. To avoid this, provide a shield by supporting the crucible in platinum foil with a hole cut in it so as to let the crucible in for about half its height. This foil, in turn, is supported by a hole in thin asbestos. When the flame is played on the lower part of the crucible, the upper part of the crucible is protected from the product of combustion. After fusion, thoroughly disintegrate the melt with water on the steam bath, preferably overnight. Filter, wash, and make up to 150–175 ml. if not already of this volume. Add enough HCl in excess of the quantity necessary to neutralize the Na_2CO_3 to make the solution about 1 per cent HCl . Bring to a boil and precipitate the sulfate with 10 ml. of a 10 per cent BaCl_2 , cool, pass through a small fine filter and wash. Ignite at a low temperature, and weigh. Occasionally, because of a long digestion, or too large an excess of acid, the silica will gel. One of the two following procedures may be adopted and should be used before the BaCl_2 is added. Remove the silica by evaporation and filtration, or remove it by precipitating the neutralized solution with ammonia. Treat ignited BaSO_4 with a few drops of hydrofluoric and sulfuric acids, cautiously ignite, and weigh again. As the reagents used invariably contain some sulfur, run blanks alongside and treat in the same manner as the determinations.

DETERMINATION OF EXCHANGE CAPACITY AND EXCHANGEABLE BASES IN SOIL—AMMONIUM ACETATE METHOD

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Procedures for determining exchange capacity and exchangeable cations have attracted much attention in recent years, in keeping with the increased recognition of the importance of the absorptive complex of the soil. In general, the methods that have been used indicate similar magnitudes for the quantities of the cations exchanged and usually rank the exchangeable cations in similar orders of importance. Notable exceptions are in aluminum and hydrogen exchanged and in exchange capacity. Exact equivalence cannot be expected by all methods. In these surface and interplanar substitutions, physical factors such as ionic radius may be important, as well as chemical properties such as the hydration of ions. Differences in tendency toward hydrolysis and in solubilities of possible compounds affect the ease of replacement or removal of the various cations. Because of effects upon hydrolysis and hydrogen-ion activity, the associated anions may have great influence, particularly upon indications for exchange capacity and hydrogen exchanged. As with most other "available" constituents, a determination of exchange capacity and of cations exchanged between a soil and a salt solution is not very exact in the quantitative sense. The probable reason is slowness in attaining equilibrium between coarse soil grains and mineral particles and solutes, and the indefinite nature of that equilibrium from the possibility of further reactions with colloidal constituents in the humus-silica-sesquioxide-base-acid-salt solution system. Fortunately, rough indications are sufficient for practical purposes and greater importance may be attached to convenience in the analytical operations.

The exchange capacity of a soil is less definite than the quantity of most of the individual cations exchanged, exclusive of hydrogen, because the latter is included in the former. The amount of hydrogen exchanged by a soil depends to a great extent upon the pH at equilibrium. Just as with a polybasic acid like phosphoric, with successive hydrogens decreasing in tendency to ionize, the successive hydrogens of the soil complex become active as pH increases. To define exchange capacity, it is necessary to select some definite pH as the point of reference or "neutrality." As to what this point should be, there are differences of opinion. Some consider pH 8.4 the proper reference point, because it is the pH of equilibrium in the system calcium-carbonate-water-carbon-dioxide at the partial pressure of the atmosphere. But there seem to be equally cogent reasons why pH 7 should be the point of reference, entirely aside from the fact that it is the conventional "neutral point." This is near the pH of the bicarbonate-carbonic-acid buffer system at partial pressures of carbon dioxide likely to prevail in the atmosphere of a fertile soil during the season of active growth. The drainage water from a soil sufficiently supplied with basic material for good

growth of most crop plants is usually near pH 7, and the available information indicates that a soil reaction of pH 6.5 to 7.0 is most favorable to crop production in general.

A point not always appreciated in discussions of exchange capacity is the difference in pH of pure "neutral salt" solutions, the effect of hydrolysis. For example, a normal solution of ammonium chloride, a salt with slightly dissociated base and strongly dissociated acid, is at pH 4.6, and the equivalent solution of potassium acetate—highly dissociated base and weakly dissociated acid—is at pH 9.4. It is evident that determinations of exchangeable hydrogen in a soil by the use of these solutions would give quite different indications. And although normal solutions of potassium chloride and of ammonium acetate are both at pH 7 because in these combinations base and acid are equally dissociated, the results with these salts would again be different. In the first comparison, the difference in pH would account for the results; in the second, an obvious explanation is that the weak soil acids or base absorbents must compete for strong and weak bases respectively against strong and weak acids. For the foregoing reasons, it seems logical to determine exchange capacity and exchangeable bases by using a solution of a neutral salt without tendency to hydrolyze; both acid and base should be weakly dissociated. A common salt that seems to meet most of the requirements is ammonium acetate.

Prianishnikov appears to have been the first to use ammonium acetate for estimating exchangeable bases in soils (5), but his paper was generally overlooked prior to a publication from this laboratory (8). Besides the theoretical advantages mentioned, this salt has in its favor the facts that ammonium is never naturally a major soil base but can function as such under laboratory conditions and is easily determinable, and the acetates of all soil bases are readily soluble. Moreover, it has the outstanding analytical advantage of being almost completely volatile at a comparatively low temperature. Every trace can be removed by ignition or treatment with suitable reagents. A solution of the highest purity is easily prepared from inexpensive reagent chemicals. About its only defects in application to base-exchange work on soils are the difficulty in titrating an excess of acid or base in a large volume of the strong solution, and its solvent effect upon calcareous material, which is greater than that of barium chloride, for example.

Ammonium acetate in solution has, to some degree, an effect upon the surface tension of water similar to that shown by the fatty acid salts of the alkali metals. It has wetting and penetrating powers superior to those of a barium chloride solution, for example. This aids in the removal of exchanged cations by leaching. Leaching seems to be the logical procedure, for it subjects the soil to the action of a continuously renewed solvent containing no constituents already extracted; an efficient leaching process should result in complete removal of exchangeable bases and equilibrium with the unchanged solvent solution in minimum time and with a minimum volume of solution. At sufficiently high concentration, aqueous ammonium acetate at pH 7 has not shown any troublesome tendency to disperse clay soils; the leaching has not been noticeably slower than might be expected with a dilute acid or other salt solution.

PREPARATION OF SAMPLE

Most of the exchangeable bases of a soil will not be appreciably affected by rapid air-drying, as is customary in the preparation of soil samples for analysis. The importance of possible slight changes in carbonate content, either from carbonation by exposure of a highly basic soil or by precipitation of solid carbonate from bicarbonates previously in solution, is probably negligible. Exchangeable ammonium is easily lost from a soil while drying in the air, but normal soils contain only traces. Under exceptional conditions, manganese may be an important exchangeable base and reverts to nonexchangeable forms very rapidly during drying (10). This may possibly be true also of ferrous iron. As these cations seldom play a major rôle, however, the question is largely academic. If there is doubt about it, the soil should be examined promptly at its field moisture content, with no preparation other than passage through a 2-mm. sieve, if possible, and sufficient mixing for uniformity. A moisture determination on the sample as weighed out for leaching will be necessary for correction to the air-dry state, the general basis of comparisons.

Air-drying the field sample will be the usual practice. The borings are spread thin on paper-lined trays and dried rapidly in a current of air at room temperature, lumps being turned and crushed if necessary. Large stones and debris are picked out and saved for further examination, especially if they are of a calcareous nature. In this laboratory, the dried samples are run through a mill, improvised from a common laundry wringer with large soft rolls, set moderately tight and mounted horizontally with a simple wooden hopper arranged to feed the soil to the rolls, which are turned by a hand crank. The rubber rolls have some shearing action and are effective in reducing lumps of all but the stiffest clays, but have minimum effect upon soft concretions. The crushed soil is sifted on a 2-mm. sieve and the residue put through the rolls again, if it seems necessary. Some clay soils will require crushing with a rubber-tipped pestle. When the residue is reduced to fairly clean stones and concretions, its ratio by weight to the whole sample is noted and it is set aside for possible further examination. The crushed and sifted soil is tumbled in a large can to mix. If the sample is too large, it is reduced by the use of a sample splitter or riffle, in preference to quartering. With samples showing a tendency to segregate, the final portion for leaching should be taken by riffing down to approximately the desired weight, e.g., 100 gm., which portion is weighed accurately. The use of such large samples may seem extravagant of time and reagents, but because of the nature of the leaching operation is not unduly so. When a complete analysis of the leachings is not to be made, it may be preferable to use a smaller sample.

APPARATUS

Leaching apparatus. A simple filter tube of conventional form has been a satisfactory container for soil to be leached. The dimensions are 40 mm. inside diameter, 120 mm. height of body, with stem 50 mm. long. This tube easily holds 100 gm. of an average mineral soil, air-dried and sifted to pass 2 mm. The assembly shown in figure 1 consists of two 1-liter Erlenmeyer flasks and the filter tube, connected by rubber parts and glass tubes, bent as shown, to form a closed system. Both leaching solution and leachate are thereby protected, minimizing the possibility of change in pH from loss of ammonia or absorption of carbon dioxide. A change from the original arrangement (11) is the substitution of a small pledget of absorbent cotton lightly stuffed into the stem of the filter tube for the porcelain plate and filter disc. This is more effective in preventing the accidental passage of soil grains and does not have any tendency to cause the filter tube to crack.

A setup convenient for leaching 10-20-gm. samples of soil, but less suitable for the determination of exchanged hydrogen and exchange capacity because the leaching solution is more exposed to the atmosphere, is shown in figure 2. The carbon filter tube is 30 mm. inside diameter, with body 85 mm. and stem 70 mm. long. The leaching time for heavy soils can be decreased by making the tube below the funnel longer, thus adding slight pressure, or the rate of flow through light soils can be decreased by adjusting the screw clamp X. Determinations of exchangeable hydrogen and exchange capacity may be made on separate samples by the methods of Brown (3).

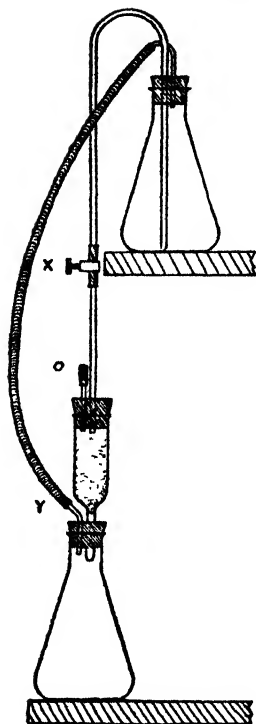


FIG. 1

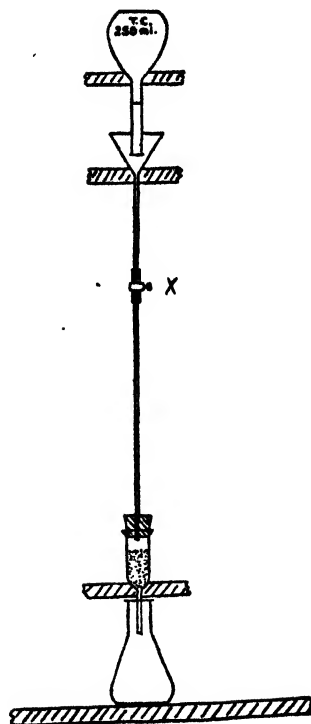


FIG. 2

FIG. 1. CLOSED-SYSTEM ASSEMBLY FOR LEACHING LARGE SAMPLES OF SOIL

O, rubber cap; X, screw clamp; Y, air return tube

FIG. 2. APPARATUS FOR LEACHING SMALL SAMPLES OF SOIL

X, screw clamp for adjusting rate of flow of leaching solution

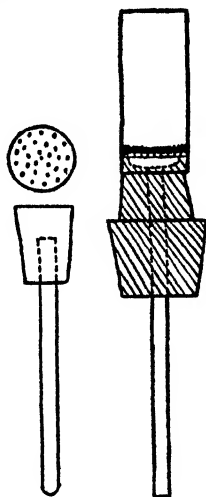


FIG. 3. SHIMER FILTER

Filter. A simple assembly convenient for suction filtration and washing of precipitates such as calcium oxalate or magnesium ammonium phosphate subsequently to be titrated is shown in figure 3. This "Shimer filter" is old but does not seem to be well known to the present generation of chemists. It is not mentioned in textbooks on analytical procedures, and no reference to the original description is known to the writers. A perforated porcelain filter disc 22 mm. in diameter fits accurately a straight-sided glass tube 50 mm. long. A no. 4 rubber stopper with central perforation is countersunk at the smaller end, leaving a narrow rim to support the porcelain disc in the tube with the stopper inserted. A large stopper fitting the suction filter flask or Witt jar is attached to the first stopper, base to base, by a suitable length of glass tubing. A tamper is made from a no. 2 stopper with glass rod handle as shown. To use this assembly for a filtration, a disc of filter paper cut with a wad cutter of the proper size is placed on the porcelain disc and wetted. Sufficient asbestos suspension is poured in to make a pad about 1 mm. thick after being lightly compacted with the tamper. After this filter has been washed several times with water, drawn through rapidly, the receptacle for the filtrate is put in place, the precipitate stirred up, and filtration begun. Washing is rapid and complete. The tube with asbestos pad and precipitate is then detached (the porcelain disc should adhere to the paper and come away from the stopper), and the tamper is inserted at the bottom and pushed upward. As the damp pad rises in the tube, the wet precipitate is cleanly wiped therefrom. The asbestos pad but not the porcelain disc is allowed to fall into the beaker for titration. The asbestos will do no harm in the titration; if there is objection to the paper, it may be omitted in preparing the filter.

PREPARATION OF THE AMMONIUM ACETATE EXTRACT

Normal ammonium acetate solution. Dilute 2,500 ml. reagent ammonium hydroxide, sp. gr. 0.90, to 18 liters in a 5-gallon bottle. Titrate 25 ml. to the methyl red end point with *N* hydrochloric acid and adjust the ammonia solution accordingly, to exactly 2 *N*. Dilute 2,100 ml. reagent acetic acid, 99.5 per cent, in the same manner. Titrate 25 ml. to the phenolphthalein end point with carbonate-free *N* sodium hydroxide, and according to the indications of this titration dilute the acetic acid solution to exactly 2 *N*. A mixture of equal volumes of these solutions should result in a *N* solution of ammonium acetate, pH 7.00, ready for use.

Leaching. Stuff the end of a small pledget of absorbent cotton loosely into the stem of the leaching tube with the aid of a lead pencil, and arrange the remainder of the cotton above to form a flat pad. Allow some water to run through, to make sure that the percolation rate will not be slowed by too tight packing of the cotton. Draw the excess water through; rearrange the cotton if necessary; and pour the sample, up to 100 gm. air-dry soil sifted to pass 2 mm., into the filter tube in several portions, working each with a spatula to reduce shrinkage on wetting. Assemble the apparatus as in figure 1, placing on a shelf the upper flask with 750–1,000 ml. of the leaching solution. Remove the rubber cap at *O* and separate the air return tube at *Y*. Blow gently through the rubber tube to start the siphon. As soon as the solution is well over the surface of the soil in the filter tube replace *O* and reconnect at *Y*. The leaching should now proceed without further attention until practically all the solvent has passed through the soil. The time for leaching should be at least 4 hours but no longer than overnight, if the nature of the soil permits. If a sample leaches too rapidly, retard the rate by adjusting the screw clamp *X*.

The occurrence of water-soluble salts is not uncommon, although considerable quantities are not to be expected in well-drained soils of a humid region. On various occasions, the writers have examined Ohio soils containing toxic amounts of water-soluble aluminum or manganese with other common soil elements or sodium, as sulfate, nitrate, or chloride. The water-soluble cations in such cases are not considered exchangeable, although they would appear in a salt extract. Their removal from the sample by a preliminary leaching with water is necessary. But for normal soils, the small amounts of such elements as calcium present as water-soluble nitrate, sulfate, or bicarbonate are customarily neglected and so are included with the exchangeable bases.

DETERMINATION OF EXCHANGE CAPACITY

Exchange capacity (for ammonium from acetate at pH 7). After the ammonium acetate leaching, take the apparatus down. Stopper the flask of leachate and set it aside. Wash the upper part of the leaching tube with alcohol—either methyl or ethyl diluted to 80 per cent by volume and neutralized with ammonia to pH 7 tint of bromthymol blue. Wash other parts of the apparatus with water. Leach the soil with about 500 ml. of the neutralized alcohol as before. Draw the last of the alcohol through by suction, stopping before the soil in the tube begins to dry, for drying will cause much ammonia to be lost. Remove a suitable portion, up to half, of the alcohol-wet soil from the percolator tube with a spatula and transfer it without loss to a weighed paper on a dish.¹ Dry this rapidly, at first in the air and possibly later in the oven, and when constancy is reached, determine the weight of soil on the paper. This weight subtracted from that of the sample taken for leaching—or as it would be when dried in the same manner—gives the weight of sample used for the determination of exchange capacity. Blow this alcohol-wet portion out of the percolator into a 1-liter copper flask with water and rinsings to make the volume about 400 ml. Add sodium hydroxide for an approximately *N* solution, distill the ammonia for 45 minutes, preferably with steam, and titrate in the usual manner. A blank on the original soil—or better, that leached for the determination of exchangeable ammonium, *q.v.*—of about the same dry weight with exact correction later, is necessary. This blank will be large, as the drastic treatment causes considerable decomposition of nitrogenous organic matter, but with care the rate of decomposition is reasonably constant. A much smaller blank is obtained by distillation with magnesia or by aeration, but complete recovery of the absorbed ammonia has been difficult by these methods, and that described is preferred for rapidity and reasonable accuracy. Alternatively, the following method might be applied to the ammonium-saturated and alcohol-washed sample:

Exchangeable ammonium. Leach a suitable sample of the soil, up to 100 gm. air-dry equivalent, with approximately 0.1 *N* hydrochloric acid in the same manner as that described for leaching with ammonium acetate. Make the leachate alkaline with sodium hydroxide, and distill the ammonia and titrate in the usual manner. Each milliliter of *N* equivalent titrated corresponds to 1 mgm. equivalent exchangeable ammonium (or exchange capacity in that determination) for the weight of sample taken.

Correction for carbonate dissolved during leaching. With soils containing limestone or calcareous concretions, the leaching results in appreciable solution of the carbonate mineral. This is probably unavoidable and is known to occur even with barium chloride and similar salts, possibly through an intermediate hydrogen exchange. It is greater with ammonium salts, but less with the neutral acetate than with an acid-hydrolyzing salt like the chloride. An approximate correction for solution of carbonate can be made by drying the remaining portion of the ammonium-saturated and washed sample and determining carbonate; any decrease from the content of the original soil represents that dissolved during leaching. If the composition of the calcareous material in the soil is known, an estimate of the amounts of calcium and magnesium taken into solution may be made. Information useful in this respect might be obtained from an analysis of the 0.1 *N* hydrochloric acid leachate if that method was used in the determination of ammonium absorbed. The alkaline earths found therein should be derived from carbonates which survived the ammonium acetate leaching.

EXAMINATION OF THE AMMONIUM ACETATE EXTRACT

The ammonium acetate leachate contains the cations exchanged from the soil plus an indeterminate but presumably small amount (except for Ca and Mg

¹ This is not advisable with coarse soils tending to segregate on leaching, so that the finer part, possibly higher in exchange capacity or carbonate content, settles to the bottom during leaching. In such cases, the whole mass of soil should be thoroughly mixed in a beaker and about half by weight of the moist soil taken for the determination of exchange capacity.

taken together from calcareous material) entering by simple solution. The exchanged cations to be expected in more than trace amounts in an ammonium acetate extract of a normal soil are hydrogen, calcium, magnesium, potassium, and sodium. In amounts exceeding a trace, aluminum is rarely found; ferric iron, never. Ferrous iron is probably exchangeable from highly reduced soils but has not been encountered in the writers' experience. Exchangeable manganese commonly occurs in determinable amount and may be very abundant in a soil that has been exposed to abnormal conditions resulting in reduction of the insoluble dioxide to an active base (9). Its accumulation to the point of toxicity, together with aluminum, water-soluble as nitrate and probably sulfate, has been noted in acid mucks and sandy soils associated therewith. Quantitatively, hydrogen is the principal cation exchanged from many acid soils.

Exchangeable hydrogen. It is impractical to titrate free acetic acid in the presence of a great excess of ammonium acetate in the ordinary manner, but good results are obtainable electrometrically. The differential method formerly used in this laboratory (11) requires the addition of quinhydrone to the solution, and for this reason the glass electrode method recently described by Brown (3) is preferable. The titration need not actually be performed; by comparing the leachate pH with that of the original leaching solution, both determined under identical temperature conditions, a good estimate of the free acid in a known volume of leachate can be made from a graph (3). To make the titration, *N* ammonium hydroxide is added from a buret to the entire amount of leachate until the pH indicated is that of the original leaching solution as determined under identical conditions; 1 ml. *N* NH_4OH required corresponds to 1 mgm. equivalent of hydrogen exchanged by the sample. In this procedure, it is advisable to make both pH determinations or the titration with an ammonium nitrate bridge attached to the usual saturated potassium chloride bridge employed in electrometric measurements, to avoid the possibility of potassium's entering the solution. With the high amplification necessary in a glass electrode setup, a very tight ground glass plug junction is practical and a slight leakage of ammonium nitrate into the solution will not be objectionable.

Evaporation and purification. After the determination of exchangeable hydrogen, set the solution in the same large Pyrex beaker on the steam plate or heat it over a burner. An ammonium acetate solution boils quietly, with little tendency to bump or spurt; there is no trouble from crystallizing salts creeping over the edge of the beaker. Ammonia is expelled more rapidly than the acetic acid. The solution becomes syrupy, and a crust may form on the surface, which should be broken to speed the evaporation. At steam plate temperature, a considerable residue of acetamide may remain; although this decomposition product boils at 222°C. , it gradually volatilizes with long heating. It may be driven off rapidly by heating the beaker, held with tongs over a large "soft" flame with continuous swirling and turning. The fumes may ignite, but this should do no harm if the operator is expecting it. When finally only a residue of acetate, more or less charred, remains allow the beaker to cool.³

According to the amount of residue in the beaker, add 12 ml. or more of aqua regia (1 volume concentrated nitric and 3 of hydrochloric acids, made as needed) and replace the covered beaker on the steam plate. It may be noted that if the mixture turns greenish black before it begins to boil, considerable manganese probably is present. This color

³ Complete decomposition of acetates to carbonates requires so high a temperature that it is not advisable to attempt it in glass. The concentrated solution should be transferred to a platinum dish if the total base equivalent is to be determined by a titration, as proposed by Bray and Wilhite (1), or the alkalis are determined by the method described by Salgado (6). But in such case, the ignition should not be too severe, lest alkali carbonates be volatilized.

soon disappears from the boiling mixture. Any remaining ammonium salts and other nitrogen compounds are decomposed and driven off as free nitrogen, nitrosyl chloride, etc. With a sufficient amount of aqua regia used at the start and one repetition with a smaller amount, expulsion of ammonium is certain. While considerable of the second addition of aqua regia still remains, add 5 ml. concentrated perchloric acid and continue boiling to heavy fumes, keeping the beaker covered. The remaining perchloric acid should be reduced to less than 1 ml. volume and should be water white. If there is much manganese, however, flashes of permanganate color may appear in the boiling acid. If this is observed, cease heating, as there is possible danger of loss as volatile Mn_2O_7 . Under the same circumstances, insoluble dark stains of MnO_2 may appear on the bottom of the beaker where overheated. In this case, cool and dissolve the stain in a drop of concentrated hydrochloric acid, which is driven off by more careful heating. Finally flame the beaker all over to expel excess acids and possibly a trace of ammonium adhering to the cooler upper parts. Treat similarly the watch glass which covered the beaker.

Filtration from silica. Wash down the walls of the beaker with 25 ml. hot water, replace the watch glass, and boil the solution for a minute; then filter it on a 9-cm. paper into a 250-ml. volumetric flask, with sufficient washing for quantitative recovery of soluble salts. The residue on the filter should be pure silica, usually of no interest. Make the filtrate and washings in the flask to 250 ml. at room temperature. This is solution A.

Ammonium sulfide precipitation. Pipette up to 200 ml. of solution A into a suitable Erlenmeyer flask and neutralize to methyl orange with ammonium hydroxide. Add 5–10 gm. ammonium chloride and 5–10 ml. 5 *N* ammonium sulfide. Fill the flask with water, stopper, and let stand overnight or longer. Separate precipitated aluminum hydroxide and sulfides of manganese etc. by filtration, washing with water containing hydrogen sulfide, a little ammonia and ammonium chloride, with the usual precautions against unnecessary exposure of the precipitate to the air, lest it become oxidized and its constituents reenter the solution. Roll up the washed paper and put it in the flask with 10 ml. concentrated nitric and 1 ml. 72 per cent perchloric acid; digest to destroy the paper; finally boil to heavy fumes of perchloric acid but expel no more than about a third of the latter. This digestion contains a proportionate part of the exchangeable manganese and possibly some aluminum etc. From many soils, no significant amounts of these elements will be obtained.

Aluminum. The ammonium sulfide precipitate contains virtually all the aluminum that might occur in the leachate; it may be determined in an aliquot of the digestion. Snell (13, p. 264) gives directions for its determination by the aurin tricarboxylic acid colorimetric method in approximately 0.25 *N* ammonium acetate plus other reagents that could be added to the first 25 ml. of leachate containing most of the aluminum which might be extracted from a 10-gm. soil sample by leaching with neutral normal ammonium acetate solution. This direct determination in a separate leachate may be preferable.

Manganese. The entire amount or an aliquot of the perchloric acid digestion of the sulfide precipitate or an aliquot of solution A may be used, according to circumstances. The following method for oxidizing manganese to permanganic acid, an adaptation of the Sandell, Kolthoff, and Lingane procedure for manganese in steel (7), is equally good for traces or larger amounts up to 5 mgm. Mn on the scale given. Bring the portion of solution to be examined to 25 ml. volume in a 50-ml. volumetric flask. If it is a small aliquot, add concentrated perchloric acid to make the total present about 0.7 ml. of the 72 per cent acid, or near the average amount remaining after the wet digestion of the filter with sulfides. Add 1 ml. reagent phosphoric acid, sp. gr. 1.7, 1 ml. concentrated sulfuric acid, 5 ml. concentrated nitric acid, 2 ml. 0.1 *N* silver nitrate, and finally 1 gm. high-test ammonium persulfate in a fresh strong solution.* Holding the neck of the flask in the fingers, swirl it gently over a

* Ammonium persulfate solutions lose strength rapidly, and the solid reagent deteriorates on keeping. It should not be used for manganese determination if the purity is less than about 90 per cent. To assay, dissolve 1.9607 gm. ferrous ammonium sulfate in 100 ml. of a

moderate flame. After the solution has boiled for about $\frac{1}{2}$ minute, and the neck of the flask has become too hot to hold, cool to 20° C. in running water. Long heating or standing hot may result in the decomposition of permanganic acid previously formed. The solution should be brilliantly clear with a true permanganate tint proportional to the manganese content, except that a blank or trace determination may show a darker off-tint attributed to the silver.

A faint permanganate color may be matched by adding 0.1 *N* permanganate from a microburet to a blank with the same volume and reagent additions carried through the operations in an identical manner. Comparison is best made in matched colorimeter cylinders wrapped with dull black paper to exclude light from the sides. This reagent blank corrects for any off-tint and for manganese in the reagents. Phosphoric acid is especially likely to contain an appreciable amount. In this colorimetric procedure, 1 ml. 0.1 *N* permanganate addition corresponds to 1.1 mgm. Mn or 0.04 mgm. equivalent exchangeable manganese in the portion of sample represented.

If the permanganate color is very strong, the solution may be titrated with 0.05 *N* sodium arsenite-nitrite, the salts in equimolecular ratio (7).⁴ Pour the solution into a 250-ml. Erlenmeyer; drain but do not rinse the smaller flask. Add 4 ml. 0.1 *N* hydrochloric acid to inactivate the silver. Titrate slowly and carefully; it is best to use a small buret delivering single drops. At the start the rate of addition should not exceed two drops per second, falling at regular intervals into the agitated solution. When the permanganate color is nearly discharged, decrease the rate to one drop in 5 seconds and finally increase the interval of additions to 10 seconds, with agitation between them. The end point is disappearance of permanganate color, disregarding any faintly pinkish opalescence of silver chloride. At the end, rinse the 50-ml. flask with the titrated solution and pour back; an unmistakable permanganate color should be noted, requiring a fraction of a drop to discharge. One milliliter of the 0.05 *N* arsenite-nitrite should correspond to approximately 0.5 mgm. manganese; exact standardization should be against a known amount of manganese, about the same as determined and oxidized to permanganic acid with identical additions and procedure. The results are closely reproducible although the reactions may not be exactly stoichiometric.⁵ Each 27.5 mgm. manganese found in the determination corresponds to 1 mgm. equivalent exchangeable manganese in the portion of sample represented.

Calcium. If calcium and magnesium are not present in great amount, the entire filtrate from the ammonium sulfide precipitation may be used for their estimation; otherwise, a suitable aliquot of it. Acidify the solution with 10 ml. concentrated hydrochloric acid, boil to expel hydrogen sulfide, and bring to 100–200 ml. volume. Any sulfur that has separated may be disregarded. Add 5–10 ml. of a solution containing 10 per cent each oxalic and acetic acids, and tint distinctly yellow with bromocresol green. Heat to boiling with constant

cold 1 per cent by volume solution of sulfuric acid. Add a weighed portion of the persulfate, 0.3–0.4 gm., and titrate the ferrous iron remaining with 0.1 *N* permanganate, requiring x ml.

$$\frac{1.141(50 - x)}{\text{g. sample}} \quad \text{per cent } (\text{NH}_4)_2\text{S}_2\text{O}_8 \text{ in sample.}$$

⁴ 0.05 *N* arsenite-nitrite: Dissolve 1.25 gm. arsenic trioxide in a cold solution of 2.0 gm. sodium hydroxide in 15 ml. water in a glass mortar. Dilute to about 100 ml. and barely acidify with sulfuric acid. Neutralize carefully with sodium bicarbonate solution, using litmus paper as indicator. Dissolve 0.87 gm. pure sodium nitrite in this and wash into a 1-liter volumetric flask; finally dilute to volume at room temperature.

⁵ Standard manganese solution: Gently ignite in one porcelain crucible within another some crystals of pure manganous sulfate to obtain the anhydrous salt as a pinkish white powder without brownish discoloration from overheating. Dissolve 0.2750 gm. of this in water containing 1 ml. concentrated sulfuric acid and dilute to 500 ml.¹ One milliliter contains 0.2 mgm. manganese.

stirring while adding diluted ammonia dropwise until the indicator color is a pure green, approximately pH 4. If there is a large precipitate of calcium oxalate, boil with stirring a minute longer to coarsen the precipitate, then filter at once on a Shimer filter. Wash practically chloride-free with slightly ammoniacal hot water, adding the first few washings to the filtrate containing magnesium. If little or no calcium oxalate was precipitated at once, digest the mixture for several hours, with occasional addition of a drop of ammonia if necessary, to separate the small amount of calcium (4). Push the asbestos filter pad with the washed precipitate out of the detached filter tube into the beaker, stir it in 100 ml. water, add 5 ml. concentrated sulfuric acid, heat the mixture to 70° C., and titrate immediately with standard permanganate solution to a faint rose tint that does not fade after a few seconds' thorough stirring. One milliliter *N* permanganate equivalent or 0.02004 gm. Ca corresponds to 1 mgm. equivalent Ca in the portion of sample taken. It may be noted that if manganese was totally absent from the solution in which the oxalate was precipitated (and there is no manganous ion in the permanganate solution), the reaction of the latter with oxalate will be slow in starting. This is sometimes useful as an indication of its absence; if present prior to the sulfide precipitation, sufficient usually escapes the separation and falls with the calcium oxalate to start the decolorization of permanganate promptly. When the color produced by the first drop of permanganate persists, a small crystal of manganous sulfate may be added to start the reaction.

Magnesium. To the cooled filtrate and first washings of the calcium oxalate precipitate add 0.5–1.0 gm. diammonium phosphate in solution, followed by strong ammonia dropwise with constant vigorous stirring. Rub the inner walls of the beaker and strike them with the stirring rod to encourage the crystallization and adherence to the glass of the precipitated $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. After the precipitate appears, or an excess of ammonia is plainly evident, continue stirring for 2 or 3 minutes, then add one-tenth volume of strong ammonia slowly with further stirring. To prevent the escape of ammonia, set the beaker in a covered jar in a cool place overnight. Filter on a Shimer filter and wash practically chloride-free with cold water containing one-tenth volume strong ammonia. Drain the beaker well at the last washing and transfer to it the filter pad with precipitate. Set in a warm and airy but not hot place to dry. When the filter pad is dry and no odor of ammonia can be detected, add a drop or two of methyl orange indicator solution⁶ and a measured volume of 0.1 *N* hydrochloric acid, in excess sufficient to preserve a strong red color after the filter pad has been dispersed and the entire inner surface of the beaker has been wetted with the acid spread with a stirring rod. Titrate the excess acid to a clear lemon-yellow tint with 0.1 *N* sodium hydroxide. Of the acid consumed by the phosphate, in effect a titration of tribasic to monobasic phosphate, 1 ml. *N* hydrochloric acid equivalent or 0.01216 gm. Mg represents 1 mgm. equivalent Mg in the portion of sample taken.

Potassium. Pipette a suitable aliquot, 25 ml. or more, of solution A into a 100-ml. beaker, evaporate, and drive off excess perchloric acid by heating directly over a "soft" flame the uncovered beaker held with tongs and kept in constant motion. Take care that the residue is not excessively heated and that none is lost by decrepitation. When cooled, add 1 ml. *N* equivalent nitric acid and water to 10 ml. total volume. The resulting solution should be clear. Next add a freshly made and filtered solution containing 1 gm. reagent sodium cobaltinitrite in 5 ml. water, stir well and let stand covered at room temperature for 2 hours. The deep yellow, heavy crystalline precipitate is of definite composition, $\text{K}_2\text{NaCo}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$ with 17.22 per cent potassium, when precipitated as described and dried at 110° C., and the precipitation of potassium is complete within the range 2–15 mgm. K, according to Wilcox (14). The precipitate can be collected and weighed in a porous bottom or Gooch crucible, previously dried and weighed, after transferral and washing 10 times with 0.01 *N* nitric acid, 5 times with 2-ml. portions of 95 per cent ethyl alcohol, sucked dry and air-dried

⁶ Not all the methyl orange sold is suitable for indicator use, and the solution deteriorates when kept. About as much of the powder as will equal in bulk half a wheat grain may be dissolved in 10 ml. water for use when needed.

previous to oven-drying for an hour, for a gravimetric determination. Titration with standard permanganate is an alternate procedure and there are good colorimetric methods (13). Each 0.0391 gm. K found represents 1 mgm. equivalent potassium in the portion of sample taken.

The old and reliable chloroplatinate method for potassium determination is also applicable, as there is no interference by perchlorate, and the absence of ammonium is assured. It may be noted also that a primary separation and gravimetric determination of potassium as perchlorate is possible; this salt is insoluble in 97 per cent ethyl alcohol, and all other perchlorates likely to be present are freely soluble in that medium (12, p. 351). Any sulfate could be precipitated by addition of barium, and silica, barium sulfate, and potassium perchlorate all weighed together, and the loss in weight after washing out the latter with hot water could be determined. Other elements could be determined in a solution obtained by suitable treatment of the alcoholic filtrate.

Sodium. A suitable aliquot of solution A, 25 ml. or more, is evaporated as described for the potassium determination. The residue is dissolved in 5 ml. water, and should be clear. Add to the cold solution 30 ml. zinc uranyl acetate solution⁷, and stir vigorously for 2 minutes, longer if no precipitate of triple acetate crystals appears. Let stand covered for 30 minutes at room temperature. Filter on a fritted glass or ordinary Gooch crucible with asbestos, previously washed and dried as for the determination and weighed. Catch the filtrate in a test tube placed in the suction flask and use this to transfer the precipitate to the crucible, with the aid of a stiff feather suitably trimmed. Wash the precipitate several times with 2-ml. portions of reagent solution and about six times with similar portions of 95 per cent alcohol shaken with triple acetate crystals immediately before use and filtered. Wash once with plain alcohol. Suck dry and let stand until the odor of alcohol has disappeared, then dry in an oven at 105° C. and weigh. The precipitated crystals dried as described contain 1.5 per cent sodium; 0.023 gm. Na found is equivalent to 1 mgm. equivalent exchangeable sodium in the portion of sample taken. A blank should be run on the ammonium acetate solution.

REFERENCES

- (1) BRAY, R. H., AND WILLHITE, F. M. 1929 Determination of total replaceable bases in soils. *Indus. Engin. Chem., Analyt. Ed.* 1: 144.
- (2) BROADFOOT, W. M., AND BROWNING, G. M. 1941 Factors influencing determination of sodium in plant material. *Jour. Assoc. Off. Agr. Chem.* 26: 916-926.
- (3) BROWN, I. C. 1943 A rapid method of determining exchangeable hydrogen and total exchangeable bases of soils. *Soil Sci.* 56: 353-357.
- (4) CHAPMAN, H. D. 1928 The precipitation of calcium oxalate in the presence of iron, aluminum, titanium, manganese, magnesium and phosphate, with special reference to the determination of total soil calcium. *Soil Sci.* 26: 479-486.
- (5) PRIANISHNIKOV, D. N. 1913 Quantitative Bestimmung der im Boden vorhandenen absorptiv gebundenen Basen. *Landw. Vers. Sta.* 79-80: 667-680.

⁷ Prepared as directed by Broadfoot and Browning (2). Dissolve 365 gm. uranyl acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, in 1,790 ml. water with the aid of heat. When solution is complete except for cloudiness, add 205 ml. 99.5 per cent acetic acid. Similarly, dissolve 1,095 gm. zinc acetate, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, in 1,242 ml. water and add 34 ml. 99.5 per cent acetic acid. Mix the two solutions hot, and when nearly cold add 0.2 gm. of the pale yellow crystalline sodium zinc uranyl acetate, as obtained in the determination, to ensure saturation. About 24 hours before the solution is needed, draw off the amount required, if settled clear, or filter, and add 15 per cent by volume conc. nitric acid. Filter the solution again immediately before use. It seems inadvisable to prepare the complete solution in amount greater than will be needed at once, as a heavy crop of large crystals separates a few days after the addition of the nitric acid.

- (6) SALGADO, M. L. M. 1934 A critical examination of analytical methods used in the determination of exchangeable potassium and sodium of soils. *Soil Sci.* 37: 39-48.
- (7) SANDELL, E. B., KOLTHOFF, I. M., AND LINGANE, J. J. 1935 A modified persulfate-arsenite method for manganese (steel analysis). *Indus. and Engin. Chem., Analyt. Ed.* 7: 256-258.
- (8) SCHOLLENBERGER, C. J. 1927 Exchangeable hydrogen and soil reaction. *Science* 65 (1692 n.s.): 552-553.
- (9) SCHOLLENBERGER, C. J. 1928 Manganese as an active base in the soil. *Soil Sci.* 25: 357-358.
- (10) SCHOLLENBERGER, C. J. 1930 Effect of leaking natural gas upon the soil. *Soil Sci.* 29: 261-266.
- (11) SCHOLLENBERGER, C. J., AND DREIBELDIS, F. R. 1930 Analytical methods in base-exchange investigations on soils. *Soil Sci.* 30: 161-173.
- (12) SCOTT, W. W. 1918 Standard Methods of Chemical Analysis, Ed. 2. New York.
- (13) SNELL, F. D., AND SNELL, C. T. 1936 Colorimetric Methods of Analysis, Vol. 1, Inorganic. D. Van Nostrand Co., Inc., New York.
- (14) WILCOX, L. V. 1937 Determination of potassium by means of an aqueous solution of trisodium cobaltinitrite in the presence of nitric acid. *Indus. and Engin. Chem., Analyt. Ed.* 9: 136-138.

DETERMINATION OF EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY OF SOILS—RAPID MICROMETHODS UTILIZING CENTRIFUGE AND SPECTROPHOTOMETER

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A knowledge of the total cation-exchange capacity and the amounts of the different exchangeable cations present in the soil is indispensable in most studies dealing with the chemical and physical behavior of the soil or with soil fertility. In view of the small amounts of exchangeable metal cations usually found, especially in acid and sandy soils, the determination of their amounts by the more conventional macromethods is attended by considerable analytical difficulties necessitating the use of a rather large soil sample and a large volume of the extracting solution. The need for more rapid methods to permit periodic analyses of soils in soil-fertility and soil-survey studies has led to the development of the rapid micromethods herein described. By use of these methods the time required to make the necessary routine determinations has been greatly reduced without significant sacrifice of accuracy. The systematic outline of the chemical analysis presented in this paper is essentially the same as that previously reported (7) except that colorimetric methods for the microdetermination of sodium and ammonium are also included in the present scheme.

The exchangeable cations are extracted with *N* ammonium acetate solution. After the excess of ammonium acetate is washed out with 95 per cent ethyl alcohol, the adsorbed ammonium, which affords a measure of the exchange capacity, is extracted with 10 per cent sodium chloride solution and determined colorimetrically by direct nesslerization. The ammonium acetate extract containing the exchangeable cations is evaporated to dryness; the organic matter and the ammonium salts are destroyed by digestion with nitric and hydrochloric acids, followed by ignition at 390° C. After evaporation with hydrochloric acid, the residue is dissolved in 0.1 *N* nitric acid. The exchangeable cations are then determined directly in separate aliquots, all of the separations being carried out in a 15-ml. centrifuge tube. Calcium is determined volumetrically as the oxalate; magnesium, potassium, sodium, and manganese are determined colorimetrically utilizing a spectrophotometer.

APPARATUS

Electric muffle with a rheostat and a pyrometer.

A centrifuge that will accommodate twenty-four 15-ml. centrifuge tubes. International Equipment Company laboratory centrifuge Size 2, Type SB, rotating at 2,000 r.p.m., has been successfully employed in centrifuging all precipitates. Centrifuging at higher speeds is likely to lead to breakage of centrifuge tubes.

A spectrophotometer or a photoelectric colorimeter provided with light filters and op-

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tical cells 1.0 cm. thick. The following Corning heat-resisting glass color filters are quite satisfactory: light red No. 2418 for magnesium determination; emerald green No. 4084 for potassium and manganese determinations; lantern blue No. 5543 for sodium and ammonium determinations. A Coleman Model 11 Universal spectrophotometer is used in this laboratory.

Pyrex 15-ml. conical centrifuge tubes graduated to contain 13 ml. (by circling with a diamond point) and numbered permanently. Another set of tubes, also graduated at 13 ml., somewhat more constricted at the tip, so that the outside diameter, measured 10 mm. from the tip, is less than 8 mm., is selected for use in the determination of magnesium.

Pyrex test tubes, 125 by 15 mm., graduated at 11 ml.

A water bath, which can be made of sheet copper, with a removable rack to hold 48 centrifuge tubes is very useful. Figure 1 shows details of construction. The removable rack permits cooling the tubes conveniently by immersion in a similar container filled with cold water. If the rack is properly constructed, the contents of the tube can be mixed without

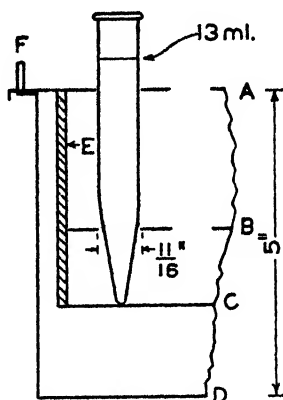


FIG. 1. SECTION OF WATER BATH

A, B, C, removable rack; D, container; E, supporting rod; F, handle. Holes in A and B are $1\frac{1}{8}$ inch in diameter and $1\frac{1}{8}$ inches apart on centers; bottom of rack C is perforated to permit circulation; dimensions of bath, 16 by 8 by 5 inches.

the use of a stirring rod by simply spinning the tube in the bath and allowing the solution to whirl inside the tube.

Another bath, consisting of a 1-liter beaker fitted with a round sheet-copper lid that supports a centrifuge-tube holder and a thermometer, is used in the permanganate titration of calcium. The titration can be thus performed at constant temperature and the end-point observed without removing the tube from the bath.

A motor stirrer for stirring the solutions in the centrifuge tubes during precipitations and, when washing, for breaking up precipitates packed by centrifuging. In addition to the motor stirrer, rods made of 3-mm. glass rod, with one end flattened to form a disk 9 mm. in diameter, are very useful for stirring the solutions by hand.

1-ml., 2-ml., 3-ml., and 10-ml. transfer pipettes.

REAGENTS, STANDARD SOLUTIONS, AND CALIBRATION CURVES

Extraction, and the determination of exchange capacity. All chemicals, unless otherwise specified, are of reagent-grade quality.

Ammonium acetate, N, pH 7.0. Prepare a sufficient volume, preferably in a Pyrex bottle, by mixing 70 ml. of ammonium hydroxide, specific gravity 0.90, and 58 ml. of 99.5

per cent acetic acid per liter of solution desired. After cooling, adjust exactly to pH 7.0 and dilute to the mark with water. It is advantageous to prepare 46 liters of this solution at a time in a 12-gallon Pyrex bottle previously marked at the 46-liter level.

Ethyl alcohol, U.S.P., 95 per cent. Test for acidity as follows: Mix 50 ml. of alcohol with 35 ml. of CO₂-free water, add a few drops of phenolphthalein, and titrate with 0.1 *N* sodium hydroxide to a slight pink color. Not more than 0.1 ml. of the sodium hydroxide solution should be required.

Sodium chloride solution, 10 per cent. Aqueous 10 per cent solution of sodium chloride, U.S.P. (ammonia-free), acidified with hydrochloric acid to render the solution approximately 0.005 *N* with respect to acidity.

Sodium tartrate, 10 per cent. Dissolve 100 gm. of sodium tartrate (Na₂C₄H₄O₆·2H₂O) in water and dilute to 1 liter.

Nessler reagent. This reagent is prepared according to Vanselow (13). In a 1-liter volumetric flask, dissolve 45.5 gm. of mercuric iodide and 35.0 gm. of potassium iodide in as little water as is needed. Add 112 gm. of potassium hydroxide, mix well, cool, and dilute to 1 liter with water. Allow to settle for a few days and use the supernatant liquid. Store in a brown glass bottle.

Standard ammonium chloride solution and calibration curve. Dissolve 1.337 gm. of ammonium chloride in ammonia-free water and dilute to 500 ml. Preserve this solution by adding 1 ml. of chloroform. For use in the preparation of the calibration curve, dilute 5 ml. of the above stock solution to 500 ml. One ml. of the diluted solution contains 0.0005 m.e. of ammonia. Measure aliquots of this solution, containing from 0 to 0.015 m.e. of ammonium, into a series of 125-ml. Erlenmeyer flasks, add 0.5 ml. of 10 per cent sodium chloride solution, dilute with water to 46 ml., add 1 ml. of 10 per cent sodium tartrate solution, and proceed with nesslerization as directed under the procedure for ammonia in the determination of the exchange capacity. Construct a calibration curve by plotting the transmittancies of the standards against concentration (milliequivalents of ammonium) on semilogarithmic graph paper.

Removal of organic matter and ammonium salts. Fuming nitric acid, sp. gr. 1.49; hydrochloric acid, sp. gr. 1.18; hydrogen peroxide, 30 per cent; dilute hydrochloric acid (1 + 1); 0.1 *N* nitric acid.

Separation of manganese, iron, aluminum, and phosphorus. Ammonium chloride, 25 per cent. Dissolve 250 gm. of ammonium chloride in water and dilute to 1 liter.

Ammonium hydroxide 0.60 *N*.

Bromine water. Saturated solution of bromine in water.

Sodium acetate, 10 per cent. Dissolve 100 gm. of sodium acetate (NaC₂H₃O₂·3H₂O) in water and dilute to 1 liter.

Methyl red, 0.02 per cent. Triturate 0.04 gm. of methyl red with 1.5 ml. of 0.1 *N* NaOH and dilute to 200 ml. with water.

Determination of calcium. Saturated solution of calcium oxalate. Saturate water with calcium oxalate, allow the excess precipitate to settle out and siphon the clear solution before use.

Ammonium oxalate, 3 per cent. Dissolve 30 gm. of ammonium oxalate [(NH₄)₂C₂O₄·H₂O] in water and dilute to 1 liter.

Hydrochloric acid, 0.5 *N*; sulfuric acid, 10 per cent.

Standard potassium permanganate, 0.025 *N* and 0.05 *N*. Dilute 0.1 *N* stock solution and standardize against sodium oxalate. The 0.025 *N* standard permanganate solution is used when the amount of calcium oxalate precipitate is very small.

Determination of magnesium. Ammonium hydroxide, concentrated sp. gr. 0.90; hydrochloric acid, 0.5 *N*.

Ammoniacal ammonium acetate wash solution. To 400 ml. of *N* ammonium acetate solution add 200 ml. of distilled water and 16 ml. concentrated ammonium hydroxide.

8-Hydroxyquinoline, 2 per cent. Prepare a fresh supply of this reagent as needed by dissolving 0.5 gm. of 8-hydroxyquinoline in 25 ml. of 95 per cent ethyl alcohol.

Phenol reagent (5). To 750 ml. of water in a 2-liter flask add 100 gm. of sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), 20 gm. of phosphomolybdic acid ($20 \text{ MoO}_3 \cdot 2\text{H}_3\text{PO}_4 \cdot 48\text{H}_2\text{O}$), and 50 ml. of 85 per cent phosphoric acid. Boil gently for 2 hours, cool, and dilute to 1 liter with water. The phosphomolybdic acid specified above is supplied by Merck & Co. The use of a reagent prepared from phosphomolybdic acid of indefinite composition, particularly with respect to water of crystallization, is likely to lead to troublesome turbidities during color development.

Sodium carbonate, 20 per cent. Dissolve 200 gm. of the anhydrous salt in water, dilute to 1 liter, and filter if necessary.

Standard magnesium quinolate solution and calibration curve. Dissolve 0.15 gm. of magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) in 100 ml. of 10 per cent ammonium chloride solution, heat to 60–70° C., add 10 ml. of the 8-hydroxyquinoline reagent, and render the solution alkaline with 4 ml. of concentrated ammonium hydroxide. Digest for 10 minutes at 60–70° C., collect the precipitate on a fritted-glass crucible, wash with hot dilute ammonium hydroxide (1 + 40), and dry at 140° C. Dissolve 0.0643 gm. of the dried precipitate in 20 ml. of 0.5 *N* hydrochloric acid and dilute to 500 ml. with water. One milliliter contains 0.01 mgm. of magnesium. Introduce aliquots of this solution, containing from 0.0025 to 0.06 mgm. of magnesium, into a series of 50-ml. volumetric flasks, dilute with water to 35 ml., and proceed with color development as directed in the procedure for magnesium. Plot the transmittancies of the standard solutions against milligrams of magnesium taken for color development on a semilogarithmic graph paper.

Determination of potassium. Ethyl alcohol, 70 per cent. Dilute 500 ml. of 95 per cent ethyl alcohol with 180 ml. of water.

Nitroso R-salt, 0.5 per cent. Dissolve 0.5 gm. of nitroso R-salt (disodium salt of 1 nitroso-2-hydroxy-3,6-naphthalene-disulfonic acid) in 100 ml. of water. When not exposed to light the reagent is stable for several weeks.

Sodium cobaltinitrite, 25 per cent. Dissolve 25 gm. of potassium-free trisodium cobaltinitrite in water, dilute to 100 ml., and filter. Store in a refrigerator when not in use. Prepare a sufficient amount of this reagent every three days or preferably as needed.

Sodium pyrophosphate, 5 per cent. Dissolve 5 gm. of powdered sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$) in water and dilute to 100 ml.

Sodium acetate, 2.5 *N*; sulfuric acid 2.0 *N*.

Standard potassium solution and calibration curve. Dissolve 0.9533 gm. of dried potassium chloride in water and dilute to 500 ml. One milliliter contains 1 mgm. of potassium. Dilute a portion of this stock solution to contain 0.5 mgm. of potassium per milliliter. Measure out aliquots of the standard solutions, containing from 0.1 to 2.0 mgm. of potassium, into a series of 15-ml. centrifuge tubes, add 0.3 ml. of *N* nitric acid, and dilute to 3 ml. with distilled water. Mix, and carry these standards through the procedure outlined for potassium. From the resultant data construct a calibration curve by plotting on semilogarithmic graph paper the transmittancies against milligrams of potassium precipitated.

Determination of sodium. Uranyl magnesium acetate reagent. Dissolve 32 gm. of uranyl acetate [$\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$] and 100 gm. of magnesium acetate [$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$] in water by warming. Cool, add 20 ml. of 99.5 per cent acetic acid and 475 ml. of 95 per cent ethyl alcohol; dilute with water to 1 liter and mix well. Filter after 2 days and store in a Pyrex bottle. The reagent is stable if kept in the dark.

Ethyl acetate-acetic acid wash solution. Dilute 300 ml. of ethyl acetate to 1 liter with 99.5 per cent acetic acid.

Ethyl ether, c.p. anhydrous.

Sulfosalicylic acid, 0.35 *N*. Dissolve 12.5 gm. of sulfosalicylic acid in water and dilute to 250 ml. Titrate a 5-ml. aliquot with 0.1 *N* sodium hydroxide, using phenolphthalein as an indicator, and adjust exactly to 0.35 *N*.

Sodium acetate, 10 per cent. Dissolve 50 gm. of sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) in water and dilute to 500 ml.

Standard sodium solution and calibration curve. Dissolve 1.525 gm. of dried sodium

chloride in water and dilute to 1 liter. One milliliter contains 0.60 mgm. of sodium. Measure aliquots of this solution, to give from 0.06 to 1 mgm. of sodium, into a series of 15-ml. centrifuge tubes. Add 0.2 ml. of *N* nitric acid, dilute with water to 2 ml., and mix the contents. Carry these standard solutions through the procedure outlined for the determination of sodium, and plot on semilogarithmic graph paper the transmittancies against the respective amounts of sodium taken for precipitation.

Determination of manganese. Sodium periodate. The more soluble sodium metaperiodate is preferred to the potassium salt. A concentrated aqueous solution of periodic acid, however, is comparatively stable and affords the addition of a readily measured volume of this reagent.

Phosphoric acid, 85 per cent.

Standard manganese solution and calibration curve. To 22.8 ml. of 0.1 *N* standard potassium permanganate in a 250-ml. Erlenmeyer flask add about 50 ml. of water and 1.0 ml. of concentrated sulfuric acid. Heat to boiling and reduce the permanganate by the addition of sodium sulfite, avoiding large excess. Boil off the excess sulfur dioxide and dilute to 1 liter. One milliliter of this solution contains 0.025 mgm. of manganese. Prepare a series of standards containing 0.005 to 0.25 mgm. of manganese in 11-ml. graduated test tubes, add 1 ml. of 85 per cent phosphoric acid, and proceed as directed under the determination of manganese. From the light transmission measurements, plot a calibration curve on semilogarithmic graph paper.

EXTRACTION, AND THE DETERMINATION OF EXCHANGE CAPACITY

Weigh a sample of soil, sufficient to give about 4 milliequivalents of total exchangeable cations, into a small Büchner funnel fitted with moist 5.5 cm. Whatman No. 42 filter paper. Leach the soil with small portions of *N* ammonium acetate at a time, using gentle suction, and catch the filtrate in a 250-ml. Pyrex beaker.² Continue to leach the soil until about 225 ml. of filtrate has been collected. (Usually 24 soil samples are analyzed simultaneously.) After the leaching, place the beaker containing the ammonium acetate extract on a hot plate and allow to evaporate to dryness. Wash the soil on the Büchner funnel with small portions of 95 per cent ethyl alcohol, draining well between additions, to remove the excess of ammonium acetate. After 150 ml. of alcohol has been leached through the soil, drain the excess of alcohol by applying gentle suction for a few minutes but do not allow the soil to dry and crack. Discard the alcohol washings. Extract the adsorbed ammonium by leaching the soil with acidified 10 per cent sodium chloride solution, adding small portions at a time, until about 225 ml. of filtrate has been collected. Transfer the sodium chloride extract to a 500-ml. volumetric flask, make up to volume with water, and mix thoroughly. Pipette a 1-ml. aliquot of the sodium chloride extract into a 125-ml. Erlenmeyer flask; add 45 ml. of water, 1 ml. of 10 per cent sodium tartrate solution, and 2.5 ml. of Nessler reagent, mixing well after each addition. After 25 minutes measure the transmittancy of the solution³ at 410 $m\mu$ (see suggested color filters under "Apparatus").

For a 25-gm. sample of soil and 1-ml. aliquot of the sodium chloride extract, the milliequivalents of ammonia found $\times 2,000$ = exchange capacity, milliequivalents per 100 gm. of soil.

Determination of exchange capacity by direct distillation of adsorbed ammonium; procedure for calcareous soils. After washing the soil with alcohol to remove the excess of ammonium acetate, transfer the soil with the filter paper to a Kjeldahl flask, add 400 ml. of water, about 10 gm. of sodium chloride, 5 drops of antifoam mixture (equal parts of mineral oil and caprylic alcohol), and 15 ml. of *N* sodium hydroxide. Connect the flask with the con-

² "Witt" filter jars are used instead of customary filter flasks, thus obviating the necessity of transferring the filtrate.

³ Here, and in all subsequent measurements, distilled water is set at 100 per cent transmittancy.

denser and distill 200 ml. into 30 ml. of 0.2 *N* standard acid. Titrate the excess acid with 0.1 *N* sodium hydroxide using methyl red indicator.

For a 25-gm. sample of soil, milliliters of 0.2 *N* sulfuric acid consumed $\times 0.8$ = exchange capacity, milliequivalents per 100 gm. of soil.

Remarks. To provide the amounts of the various constituents within the range that can be handled conveniently by the methods under consideration, the weight of the soil sample taken for extraction should be varied with the exchange capacity. This can be roughly estimated from soil texture and the apparent organic matter content. Air-dried soils that have been stored for a long time and that are difficult to wet should be allowed to stand overnight in contact with about 50 ml. of ammonium acetate prior to leaching.

Although tests with slightly calcareous soils have shown no loss of ammonia from the alkaline sodium chloride extracts during filtration under reduced pressure, some loss of ammonia may be incurred in the extraction of highly calcareous soils. In such soils the adsorbed ammonium should be determined by direct distillation, subsequent to washing with alcohol.

The excess of ammonium acetate is generally removed by washing with alcohol previously neutralized with ammonium hydroxide in order to prevent the loss of the adsorbed ammonium. Chapman and Kelley (2) employed methyl alcohol neutralized with ammonia, whereas Schollenberger (10) recommended the use of 80 per cent ethyl alcohol adjusted to pH 7.0 with ammonia and bromthymol blue as the indicator. The A.O.A.C. ammonium adsorption method (1) for the determination of exchange capacity specifies 95 per cent ethyl alcohol without the addition of ammonia. The loss of the adsorbed ammonium upon washing with 95 per cent ethyl alcohol with and without the addition of ammonia has been reinvestigated recently by Shaw (12), who found that the exchange capacity was higher by 2 to 4 m.e. per 100 gm. of soil when neutral alcohol was used to which 2.5 ml. of *N* ammonium hydroxide per liter of 95 per cent ethyl alcohol had been added. He concluded that "the practice of ammoniating alcohol wash may cause enhanced and variable absorption values." Although prolonged washing with nonammoniated 95 per cent ethyl alcohol may cause appreciable losses of the adsorbed ammonium, the higher values for exchange capacity obtained by use of neutral alcohol, as commonly adjusted with ammonia to pH 7 using brom thymol blue indicator, may be attributed in part to further adsorption of ammonium by the soil during the washing process. Neutralization of alcohol with ammonia using brom thymol blue as the indicator is indeed quite meaningless, inasmuch as the alcohol decreases significantly the dissociation constant of both the indicator and ammonium hydroxide. According to Kolthoff and Furman (6, pp. 101-102), indicator acids in alcohol solution will become more sensitive to hydrogen ions and their color change will be shifted to considerably higher pH values. Thus the color of brom thymol blue will turn yellow in alcohol even in the absence of any free acid. Because the dissociation of ammonium hydroxide is also reduced in alcohol solution, an appreciable amount of ammonium hydroxide must be added to effect the proper color change of brom thymol blue. The pH measurements with the glass electrode are also subject

to large errors in concentrated alcohol solutions (4, p. 142). In light of these considerations, the writer has recently adopted 95 per cent ethyl alcohol without the addition of ammonia for washing the soil free of ammonium acetate. The alcohol should be tested for acidity, as directed under "Reagents." The use of ethyl alcohol wash solutions of lower concentrations, 60 to 80 per cent, is certain to cause significant losses of the adsorbed ammonium and thus lead to low values for the exchange capacity. A few preliminary trials made with 99 per cent isopropyl alcohol showed that the use of this alcohol as a wash solution gives higher values for exchange capacity than those obtained by use of ethyl alcohol.

DETERMINATION OF EXCHANGEABLE CATIONS

Destruction of organic matter and ammonium salts. After evaporation of the ammonium acetate extract, cool, cover the beaker with a watch glass, and add slowly through the lip 5 ml. of fuming nitric acid and 1 ml. of concentrated hydrochloric acid. Warm on a hot plate until the reaction has subsided and the brown fumes are no longer given off. Rinse the watch glass into the beaker, and evaporate the solution to dryness at low heat to prevent spattering. Continue to heat for about 10 minutes to dehydrate the salts, then place the beaker in an electric muffle at 150° to 200° C., heat to 390° \pm 10° C., and hold at this temperature for 15 minutes. Remove the beaker from the muffle and cool. Treat the residue with 3 ml. of dilute hydrochloric acid (1 + 1) to dissolve the oxides of manganese, iron, and aluminum, evaporate to dryness on a steam bath, and continue heating for about 15 minutes longer to dehydrate the silica. Cool and add immediately from a burette 12.5 ml. of 0.1 *N* nitric acid; stir with a rubber policeman to loosen and dissolve the residue of salts. Transfer to a 15-ml. centrifuge tube and centrifuge for 10 minutes to throw down the silica. Designate this as solution A.

Remarks. The ignition at 390° C., following the evaporation with a mixture of nitric and hydrochloric acids, assures complete expulsion of organic matter and ammonium salts without loss of any constituent to be determined. Prolonged heating and higher temperatures should be avoided to prevent volatilization of potassium and sodium. The treatment recommended will decompose ammonium sulfate completely as well as ammonium chloride and ammonium nitrate, provided the amount of sulfate is not in excess of the equivalent of the bases present. Such an excess of sulfate is, of course, never encountered. The efficacy of this gentle ignition to destroy the last traces of organic matter depends upon the presence of salts of nitric acid. Occasionally when dealing with soils extremely low in exchangeable metal cations (acid sandy soils), some carbon is formed during the ignition process. This carbon resists further ashing at 390° C. even upon repeated evaporation with nitric acid and ignition, but may be partly destroyed by evaporation with 1 ml. of 30 per cent hydrogen peroxide. With soils high in exchangeable manganese, the residue from the ignition will be dark, owing to manganic oxide which should not be mistaken for carbon. The treatment for destroying the organic matter and ammonium salts is very effective and rapid. It leaves readily soluble salts which are dissolved in a small volume of 0.1 *N* nitric acid suitable for the direct determination of the individual exchangeable cations in separate aliquots without further evaporations and ignitions. When dealing with alkali soils high in sulfate, the residue of salts cannot

be dissolved in such a small volume of 0.1 *N* nitric acid, because of the low solubility of calcium sulfate. Obviously, appropriate modifications must be introduced in the procedures herein outlined for different constituents, if it should become necessary to take up the residue in stronger acid solution. When the silica precipitate is very large, which is seldom the case, it should be washed with hot 2 per cent hydrochloric acid; the washings should be combined with the original solution, evaporated to dryness on a steam bath, and the residue redissolved in 12.5 ml. of 0.1 *N* nitric acid.

Separation of manganese, iron, aluminum, and phosphorus prior to the determination of calcium and magnesium. Transfer a 2-ml. aliquot of solution A to a 15-ml. centrifuge tube, add 3 ml. of water and 2 ml. of 10 per cent sodium acetate solution, and mix the contents; then add 1 ml. of 0.1 *N* sodium hydroxide, and mix again. Place the centrifuge tube in a water bath at 95° C., add 1 ml. of bromine water, and mix by spinning the tube in the bath and allowing the solution to whirl inside the tube. Maintain this temperature for at least 1 hour to flocculate manganese dioxide and to expel the excess of bromine. Then add 2 ml. of 25 per cent ammonium chloride solution and digest for about 15 minutes longer. Add 1 drop of methyl red, and if the color of the indicator persists, indicating complete expulsion of bromine, remove the tube from the water bath, cool, add 0.6 *N* ammonium hydroxide from a burette until the color of the solution changes to yellow, and then add 2 drops in excess. A rather constant amount, 0.5 ml., of ammonium hydroxide solution is usually required and may be added at one time. Make up to a volume of 13 ml. with water, add 5 drops in excess to allow for evaporation, mix the contents with a stirring rod, and digest in a water bath at 80° C. for 5 minutes to flocculate the precipitate. Centrifuge while hot for 10 minutes at 2,000 r.p.m. Designate the supernatant liquid as solution B.

Remarks. In the precipitation of manganese by bromine, the addition of 2 ml. of 10 per cent sodium acetate solution and 1 ml. of 0.1 *N* sodium hydroxide to the 2-ml. aliquot buffers the solution at pH 5.7, which is sufficiently high to prevent dissolution of the manganese dioxide. When dealing with soils very high in calcium, an aliquot of only 1 ml. of solution A is taken and the addition of 1 ml. of 0.1 *N* sodium hydroxide is then omitted. To preclude oxidation of the ammonium salts and consequent increase in the acidity of the solution, both ammonium chloride and ammonium hydroxide are added after the excess of bromine has been expelled. Further digestion in the presence of ammonium chloride assures the removal of the last trace of bromine, which would otherwise destroy the indicator used later. The pH of solution B is usually about 6.8. A small amount of phosphate, which may be present in excess of the equivalent of iron and aluminum and thus escape precipitation, was found (7) to cause no interference in subsequent determinations of calcium and magnesium. Because of the small amounts of manganese, iron, and aluminum extracted by ammonium acetate solution, it has not been found necessary to wash the precipitate of manganese, iron, and aluminum.

Determination of calcium. Pipette a 10-ml. aliquot of solution B into a 15-ml. centrifuge tube without disturbing the precipitate of manganese, iron, and aluminum. This is done best by holding the tube in front of a mirror while pipetting. Add 0.5 ml. of 0.5 *N* hydrochloric acid and 1 ml. of water. Place the tube in a water bath at 70° C., mix the contents by spinning the tube, add 2 ml. of 3 per cent ammonium oxalate, and mix thoroughly again.

Digest for 30 minutes at 70° C. Remove the tube from the bath and let stand for 30 minutes. Make to a volume of 13 ml. and mix thoroughly. It is seldom necessary to adjust the volume, since 0.5 ml. is provided in excess to compensate for evaporation during digestion. Centrifuge for 15 minutes at 2,000 r.p.m., decant the clear supernatant liquid into a dry test tube and save for the determination of magnesium (solution C). Allow the centrifuge tube, inverted at about a 45° angle, to drain for several minutes on filter paper, add 5 ml. of saturated aqueous solution of calcium oxalate, break up the precipitate by means of a stirring rod, wash the rod, and centrifuge for 15 minutes. Decant, discarding the clear solution, and drain the tube for several minutes. Add 5 ml. of 10 per cent sulfuric acid solution, heat to 70° C. in a water bath, and titrate with standard permanganate. If the titer is greater than 5 ml., add about 4 drops of concentrated sulfuric acid before completing the titration.

For a 25-gm. sample of soil and 2-ml. of solution A, 1 ml. of 0.05 *N* permanganate = 1.62 m.e. per 100 gm., or 650 pounds of calcium per 2,000,000 pounds of soil.

Remarks. In order to prevent coprecipitation of magnesium, calcium is precipitated at pH 5. One washing of calcium oxalate precipitate is sufficient, provided the centrifuge tube has been drained properly each time after decantation.

Determination of magnesium. Introduce a 10-ml. aliquot of the solution from the calcium determination (solution C) into a 15-ml. centrifuge tube. Place the tube in a bath at 70° C., and add 0.8 ml. of 2 per cent alcoholic solution of 8-hydroxyquinoline; mix immediately by stirring, and then add 0.4 ml. of concentrated ammonium hydroxide from a burette. Stir vigorously for 1 minute, or longer until full turbidity develops, if the amount of magnesium is extremely small. Wash the stirring rod with a few drops of water and replace the centrifuge tube in a water bath at 70° C. for 10 minutes. After digesting for 10 minutes, cool to about 25° C., and allow to stand for 45 minutes to assure complete precipitation of magnesium. (If the solution is not yellow, and very seldom it is not, the amount of the 8-hydroxyquinoline reagent added was insufficient to precipitate all the magnesium.) Wash down the precipitate by slowly adding 0.5 ml. of 95 per cent ethyl alcohol down the sides of the tube so as to form a layer of alcohol on top of the solution and thus prevent creeping of the precipitate. Centrifuge for 15 minutes at 2,000 r.p.m., and draw off by suction 2 to 3 ml. of the clear liquid from the top to remove the layer of alcohol. Decant carefully, discarding the solution, and wipe the mouth of the tube with filter paper. Add 5 ml. of ammoniacal ammonium acetate wash solution down the sides of the tube, break up the precipitate with a stirring rod, and wash off the rod into the tube; add 0.5 ml. of alcohol slowly down the sides of the tube to prevent creeping of the precipitate, and centrifuge for 15 minutes. Draw off the layer of alcohol, decant, and repeat the washing once more as directed above. Dissolve the precipitate in 4 ml. of 0.5 *N* hydrochloric acid, dilute to 13 ml. with water, stopper, and mix. Transfer a 2-ml. aliquot (use 1 ml. if the solution is distinctly yellow) to a 50-ml. volumetric flask, and add 35 ml. of water, 5 ml. of 20 per cent sodium carbonate solution and 3 ml. of phenol reagent, mixing the contents well after each addition. Place the flask in boiling water for 1 minute, remove from the bath, and allow to stand for 15 minutes. Then cool, make to volume, mix, and measure the transmittancy at 625 m μ .

For a 25-gm. sample of soil and 2-ml. aliquot of solution A, 1 mgm. magnesium precipitated = 3.48 m.e. per 100 gm. or 845 pounds of magnesium per 2,000,000 pounds of soil.

Remarks. The conditions for precipitation of magnesium outlined in the procedure have given consistently good results and should be followed closely. Although the presence of oxalate seems to inhibit complete precipitation of magnesium if the solution is not stirred sufficiently, excellent recoveries even of

small amounts of magnesium have been obtained from solutions containing large amounts of ammonium oxalate, provided the solution is stirred vigorously for about 1 minute after the addition of the reagents. Because the precipitate is light and does not pack well upon centrifuging, considerable care must be exercised in decanting the supernatant liquid in order to prevent loss of the precipitate. For this purpose, it is advisable to select centrifuge tubes that are somewhat more constricted at the tip. The precipitate shows much less tendency to break away from the bottom of the tube and proper drainage of the tubes is facilitated if the layer of alcohol is drawn off before the supernatant liquid is decanted.

Determination of potassium. Introduce a 3-ml. aliquot of solution A into a 15-ml. centrifuge tube. If more than 2 mgm. of potassium is suspected in the 3-ml. aliquot, use a smaller aliquot and dilute to 3 ml. with 0.1 *N* nitric acid. Add 1 ml. of sodium cobaltinitrite reagent and mix the contents thoroughly by swirling the tube. Stopper, and let stand in the refrigerator (10° C.) for 1 hour, then add 4 ml. of 70 per cent ethyl alcohol, mix well with a rod, wash the rod with alcohol, and centrifuge for 15 minutes at 2,000 r.p.m. Decant the supernatant liquid, drain the tube for several minutes by inverting at about a 45° angle, add 5 ml. of 70 per cent ethyl alcohol down the walls of the tube, break up the precipitate with a stirring rod, wash the rod with alcohol, and centrifuge for 10 minutes. Decant the clear solution, allow the tube to drain for several minutes, wipe the mouth of the tube with filter paper, and repeat the washing with 5 ml. of 70 per cent ethyl alcohol. Add 5 ml. of 2 *N* sulfuric acid, place the tube in a water bath at 70° C., and mix the contents occasionally by spinning the tube until the precipitate is completely dissolved; then add 5 to 7 ml. of water and heat for several minutes more to dissolve any precipitate adhering to the sides of the tube. Cool, dilute to 13 ml., stopper, and mix thoroughly. Introduce a 1-ml. aliquot of the solution into a 25-ml. volumetric flask; add 15 ml. of water, 1 ml. of 5 per cent sodium pyrophosphate solution, 1 ml. of 2.5 *N* sodium acetate solution, and 2 ml. of 0.5 per cent solution of nitroso R-salt, and mix well after each addition. Dilute to 25 ml., mix well, and after 20 minutes measure the transmittancy of the solution at 530 $m\mu$.

For a 25-gm. sample of soil and 3-ml. aliquot of solution A, 1 mgm. of potassium found precipitated = 0.426 m.e. per 100 gm., or 333 pounds of potassium per 2,000,000 pounds of soil.

Remarks. In developing the cobalt color with nitroso R-salt, it is important to control the pH of the solution. The color fails to develop below pH 3, but develops slowly between pH 3 and 4. Between pH 4 and 5 the color develops rapidly and the intensity is constant; above pH 5 the intensity of the color increases very gradually with increase in pH. The addition of 1 ml. of 5 per cent solution of sodium pyrophosphate and 1 ml. of 2.5 *N* sodium acetate solution to the 1-ml. aliquot of the solution of the cobaltinitrite precipitate buffers the final solution strongly at pH 5. Sodium pyrophosphate was found effective in preventing the interference from small amounts of iron which might precipitate as the phosphate together with the potassium cobaltinitrite and which would react subsequently with the nitroso R-salt to impart a greenish cast to the final color developed.

Determination of sodium. Pipette a 2-ml. aliquot of solution A, containing 0.06 to 1 mgm. of sodium, into a 15-ml. centrifuge tube. Add 5 ml. of uranyl magnesium acetate reagent and stir vigorously for 1 minute. Rinse the stirring rod with 0.5 ml. of the reagent, mix by

swirling the tube, and allow to stand in a water bath at 15° C. for 1½ hours. Centrifuge for 15 minutes at 2,000 r.p.m., decant, drain for several minutes, and wipe the mouth of the tube with filter paper. Add 4 ml. of ethyl acetate-acetic acid wash solution down the sides of the tube, break up the precipitate with a stirring rod, rinse the rod with about 0.5 ml. of the wash solution and centrifuge for 10 minutes. Decant and drain; wipe the mouth of the tube with filter paper. Add 4 ml. of diethyl ether down the sides of the tube, break up the precipitate with a stirring rod, wash the rod with about 1 ml. of ether, and centrifuge for 8 minutes. Decant and drain for not more than 1 minute, as longer draining may cause dropping of the dry precipitate from the tube. Repeat the washing with 4 ml. of ether as before. Put the tube in a warm place to evaporate the last traces of ether. Dissolve the precipitate in water, dilute to 13 ml., stopper, and mix well by inversion. Centrifuge for 10 minutes to remove the trace of insoluble uranyl phosphate that may be present. Introduce a 5-ml. aliquot of the solution containing sodium uranyl magnesium acetate into a dry 25-ml. Erlenmeyer flask; add 5 ml. of water and 1 ml. of 0.35 *N* sulfosalicylic acid solution and mix; then add 1 ml. of 10 per cent sodium acetate solution and mix well again. After 15 minutes, measure the transmittancy at 450 mμ.

For a 25-gm. sample of soil and 2-ml. aliquot of solution A, 1 mgm. of sodium found precipitated = 1.09 m.e. per 100 gm., or 500 pounds per 2,000,000 pounds of soil.

Remarks. The procedure outlined for the determination of sodium is a modification of the colorimetric method described by Darnell and Walker (3). The more sensitive uranyl magnesium acetate reagent has been substituted for the uranyl zinc acetate solution in the precipitation of sodium as the triple salt. Of the two reagents, the alcoholic uranyl magnesium acetate reagent is not only more sensitive to small amounts of sodium but gives much better separation from large amounts of potassium, as shown by Piper (9), and is, therefore, more applicable to analysis of soil extracts. The smallest amount of sodium that can be precipitated completely under conditions outlined in the procedure is 0.06 mgm.; with such small amounts of sodium, however, the amount of potassium present should not exceed 2 mgm. If less than 0.06 mgm. of sodium is thought to be present in the 2-ml. aliquot, solution A should be concentrated by evaporation. As little as 0.02 mgm. of sodium may be precipitated completely if the temperature during precipitation is lowered to 5° C., but unfortunately the reagent also becomes more sensitive to potassium at this temperature, resulting in poor separation of sodium even in the presence of less than 2 mgm. of potassium. For this reason, the temperature and time of precipitation specified in the procedure should be observed closely. The ethyl acetate-acetic acid wash solution, employed by Darnell and Walker (3) for washing the sodium uranyl zinc acetate, has been found equally satisfactory for washing the sodium uranyl magnesium acetate precipitate. The use of a saturated solution of the triple salt in 95 per cent ethyl alcohol, commonly employed for this purpose, gave low and erratic results.

Determination of manganese. Transfer a 1- to 3-ml. aliquot of solution A, depending upon the amount of manganese, to a test tube graduated at 11 ml. (The amount of manganese present may be estimated roughly from the previous separation of manganese in the determination of calcium and magnesium.) Add 1 ml. of 85 per cent phosphoric acid, dilute to volume with water, adding 0.3 ml. in excess to allow for evaporation, and mix with a glass stirring rod. Place in a water bath at 95° C., add about 50 mgm. of sodium periodate, mix

thoroughly again with a glass rod, and leave in the bath for 1 hour to assure full development of the color. Cool, make to volume if necessary, mix, and measure the transmittancy at 530 m μ .

For a 25-gm. sample of soil and 3-ml. aliquot of solution A, 1 mgm. of manganese found = 0.607 m.e. per 100 gm., or 333 pounds per 2,000,000 pounds of soil.

Remarks. The use of phosphoric acid instead of sulfuric acid, often employed, in the oxidation of manganese by periodate offers several advantages. The oxidation of manganese, regardless of the amount present, proceeds very rapidly in phosphoric acid solution over a wide range in acidity without the occasional formation of off-color tints due to precipitation of manganese. Precipitation of calcium sulfate is also obviated. The practice of adding persulfate to destroy traces of organic matter, even a few minutes prior to the addition of periodate, is certain to cause precipitation of manganese, especially at higher concentrations, and should be avoided. The small amount of organic matter that may be present at this stage, as a result of incomplete ashing, has not been found to cause serious trouble. Inasmuch as an excess of periodate is added, the small amount of chloride present does not interfere and need not be removed.

COMMENTS

The amount of exchangeable hydrogen in acid soils is computed by subtracting the sum of exchangeable calcium, magnesium, potassium, sodium, and manganese from the exchange capacity. Because of the appreciable solubility of calcium carbonate in ammonium acetate solution, the exchangeable calcium content of saturated soils containing an excess of calcium carbonate is also obtained by difference, *i.e.*, by subtracting the sum of the exchangeable cations, excluding calcium, from the exchange capacity. Obviously, the results for exchangeable calcium and magnesium will be in error by this method of computation if carbonates of both calcium and magnesium are present. In such soils, the sum of calcium and magnesium may be obtained indirectly by subtracting the sum of potassium, sodium, and manganese from the exchange capacity as determined by the ammonium adsorption method. This procedure is also open to some criticism. The incomplete replacement of the adsorbed calcium and magnesium by ammonium acetate in the presence of large amounts of calcium and magnesium carbonates, as shown by Chapman and Kelley (2) and Shaw (12), will lead to somewhat low values for the exchange capacity and for the sum of calcium and magnesium as obtained by difference. Shaw (12) recently reconsidered the problem of accurate determination of exchangeable calcium and magnesium in calcareous soils and concluded that the most logical and accurate procedure for soils containing appreciable quantities of carbonates of calcium and magnesium is to effect complete extraction of the adsorbed cations and carbonates by the boiling ammonium chloride procedure (11) and to deduct the carbonate equivalence. Although this procedure permits accurate determination of the exchange capacity by the ammonium adsorption method and thus gives indirectly the correct value for the sum of exchangeable calcium and

magnesium of soils containing calcium and magnesium carbonates, proper assignment of the carbonate equivalence to calcium and magnesium is impossible.

Because of the small amounts of iron and aluminum usually found in ammonium acetate extracts, no provision has been made for the determination of these two constituents. With slight modifications, the colorimetric procedures for iron and aluminum previously described (8) should be applicable to the present scheme.

"Blank" determinations should be made on reagents from time to time. A standard synthetic soil solution is often carried through the procedures simultaneously with a series of soil extracts.

SUMMARY

Systematic time-saving microprocedures, especially suitable for routine analytical work, are described for the determination of the exchangeable cations and the exchange capacity of soils. The exchangeable cations are extracted with 1 *N* ammonium acetate solution. The exchange capacity is determined by direct nesslerization of the ammonium adsorbed by the soil, subsequent to extraction with sodium chloride solution. All of the separations in the analysis of the ammonium acetate extract are carried out in a 15-ml. centrifuge tube. Calcium is determined volumetrically as the oxalate. Colorimetric methods utilizing a spectrophotometer are employed in the determination of magnesium, potassium, sodium, and manganese. Because accurate determination of the small amounts of exchangeable cations by conventional macromethods is attended by considerable analytical difficulties necessitating the use of a large soil sample and a large volume of the extracting solution, the more rapid micro-methods herein described can be employed to advantage without significant sacrifice of accuracy.

REFERENCES

- (1) Association of Official Agricultural Chemists 1940 Official and Tentative Methods of Analysis, ed. 5. Washington, D. C.
- (2) CHAPMAN, H. D., AND KELLEY, W. P. 1930 The determination of the replaceable bases and the base-exchange capacity of soils. *Soil Sci.* 30: 391-406.
- (3) DARNELL, M. C., JR., AND WALKER, B. S. 1940 Determination of sodium in biological fluids. *Indus. and Engin. Chem., Analyt. Ed.* 12: 242-244.
- (4) DOLE, M. 1941 The Glass Electrode. John Wiley & Sons, Inc., New York.
- (5) FOLIN, O., AND DENIS, W. 1915 A colorimetric method for the determination of phenols (and phenol derivatives) in urine. *Jour. Biol. Chem.* 22: 305-308.
- (6) KOLTHOFF, I. M., AND FURMAN, N. H. 1926 Indicators. John Wiley & Sons, Inc., New York.
- (7) PEECH, M. 1941 Determination of exchangeable bases in soils. Rapid micro-methods. *Indus. and Engin. Chem., Analyt. Ed.* 13: 436-441.
- (8) PEECH, M., AND ENGLISH, L. 1944 Rapid microchemical soil tests. *Soil Sci.* 57: 167-195.
- (9) PIPER, C. S. 1932 The determination of sodium by precipitation as the triple salt sodium uranyl magnesium acetate. *Jour. Agr. Sci.* 22: 676-687.
- (10) SCHOLLENBERGER, C. J., AND DREIBELBIS, F. R. 1930 Analytical methods in base-exchange investigations on soils. *Soil Sci.* 30: 161-173.

- (11) SHAW, W. M. 1939 Report on the ammonium-chloride-distillation procedure for the determination of exchangeable bases in soils. *Jour. Assoc. Off. Agr. Chem.* 22: 242-248.
- (12) SHAW, W. M. 1940 Determination of exchange bases and exchange capacity of soils. *Jour. Assoc. Off. Agr. Chem.* 23: 221-232.
- (13) VANSLOW, A. P. 1940 Preparation of Nessler's reagent. *Indus. and Engin. Chem., Analyt. Ed.* 12: 516-517.

DETERMINATION OF TOTAL, ORGANIC, AND AVAILABLE FORMS OF PHOSPHORUS IN SOILS¹

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In presenting methods for determining soil phosphorus, the writers have narrowed their range in choice by requiring that the methods measure the form or forms desired with the necessary selectivity and that they do it in a sufficiently quantitative manner. It is considered that the following methods meet these requirements so far as the present knowledge of soil phosphorus permits.

TOTAL PHOSPHORUS

From among the numerous methods for determining total phosphorus in soils, the writers have selected the perchlorate digestion of Sherman (13) and the phosphate determination of Schricker and Dawson (12), as modified by Dean and Deemer.³ Its advantages are that it can be applied in a semimicro-way if desired, that the phosphorus is determined directly in an aliquot from the original digestion, and that arsenic and iron do not interfere when present in appreciable but not excessive amounts.

Reagents (phosphorus-free)

- (a) *Perchloric acid.* 60 per cent.
- (b) *Sulfomolybdic acid.* Ignite c.p. MoO_3 in a porcelain dish at dull red heat, but below the melting point, in a muffle for about 1 hour. Cool, and weigh 7.2 gm. into a 800-ml. Kjeldahl flask. Add 250 ml. of concentrated H_2SO_4 and a few glass beads, and boil the mixture until solution is complete (a slight cloudiness does not matter). Cool, and preserve in a glass-stoppered bottle.
- (c) *Standard phosphate.* Dilute 0.4389 gm. of dry KH_2PO_4 to 1 liter. One milliliter of this solution contains 100 γ of phosphorus (P). Make solutions containing 10 γ and 1 γ of phosphorus per milliliter by diluting suitable aliquots of solution.
- (d) *Sodium bisulfite.* Dissolve 5.2 gm. of c.p. NaHSO_3 in 100 ml. of $N \text{ H}_2\text{SO}_4$. Prepare the solution weekly and keep stoppered.
- (e) *Quinaldine red.* 0.01 per cent aqueous solution.
- (f) *Metol.* Dissolve 0.42 gm. of metol (*p*-methylaminophenol sulfate) and 6.3 gm. of Na_2SO_3 in water and make to 100 ml. Prepare fresh solution every 3 or 4 days.

Analytical procedure

Weigh 2 gm. of fine soil (35-mesh) into a 300-ml. Kjeldahl flask and add 30 ml. of 60 per cent perchloric acid. Digest on the hot plate under a hood for 20 minutes after the dark color due to organic matter has disappeared. At this stage heavy white fumes of perchloric

¹ Published with approval of the director of the Illinois Agricultural Experiment Station.

² Chief and associate, soil fertility, department of agronomy, respectively.

³ The writers are indebted to L. A. Dean and R. B. Deemer, Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, for permission to use this modification as described in a personal communication.

acid appear and the insoluble material becomes like white sand. An additional 1 to 2 ml. of perchloric acid may be used to wash down any black particles that stick to the sides of the flask.

When the sample is sufficiently cool to avoid spattering, dilute with distilled water and filter into a 250-ml. volumetric flask. Wash the residue to bring the volume to the mark.

Pipette an aliquot (less than 25 ml.) of the solution containing phosphorus into a 50-ml. volumetric flask. Add 1 drop of the quinaldine red and adjust with 2 *N* Na_2CO_3 or 2 *N* H_2SO_4 to the point where the red color just disappears. Add water to make a volume of 25 ml., then 5 ml. of NaHSO_4 solution, and digest in a water bath for 30 minutes (20 minutes after the temperature has reached 95° C.) with flasks partly immersed in the water. Carefully pipette 0.5 ml. of the sulfomolybdic acid reagent into the flask letting it run down the side of the neck. Pipette 2.0 ml. of the metol reagent into the flask and wash down the neck with a few drops of water. Continue the digestion in the water bath for 1 hour, cool, make to volume with water, mix and read in a photoelectric photometer.

Concentrations of iron (Fe_2O_3) greater than 5 mgm. per 50 ml. interfere, as do concentrations of silica (SiO_2) greater than 2 mgm. per 50 ml.

The photoelectric photometer readings are transformed to micrograms per milliliters by means of a chart prepared with the standard phosphate solution, the reading range being 0 to around 1.0 γ per milliliter.

AVAILABLE FORMS OF PHOSPHORUS

Tentative methods

The knowledge of the different forms of phosphorus in soils is not extensive. Recently, however, concepts about the available forms of phosphorus have been somewhat clarified by the general division of certain soil phosphates into the adsorbed forms and the easily acid-soluble forms (1-4, 10, 11, 14, 15).

Methods for determining the available forms in the past have not recognized this division. Recent work indicates that most of the methods employing acids or acids buffered to definite pH values have been extracting easily acid-soluble forms more or less effectively but have been relatively less effective in extracting the adsorbed forms except where these were present in large amounts (3). Furthermore, it has been shown that as these latter forms increase in amount their solubility in water increases rapidly.⁴ This explains why the acid reagents remove relatively more of them when they are present in high amounts. It also explains why the adsorbed forms are the most effective forms of phosphorus in the soil for plants, once adequate amounts have been built up. But when they are present in very small amounts their solubility is very low, and they then appear to be relatively ineffective (2).

To understand the function of phosphorus in soil fertility, therefore, one must measure and evaluate the different forms of phosphorus separately in research work, although in practice this may not always be necessary.

Recently, neutral ammonium fluoride was suggested as a reagent for removing the adsorbed forms of phosphate and separating them from the acid-soluble forms (8). When the acid-soluble forms are first dissolved in acid without

⁴ Kurtz, L. T. 1943 Adsorption and release of phosphate ions by soils and clays. [Unpublished doctor's thesis. Copy on file Univ. Illinois, Urbana.]

extracting and then an extraction with ammonium fluoride is made, both forms are extracted, and the acid-soluble forms can be calculated by difference.⁵

Studies with these methods on corn belt soils have shown that both groups of forms occur generally in these soils. In untreated soils below a pH of 6.0 the adsorbed forms are relatively more abundant than at higher pH values. Added soluble phosphates change into these forms, whereas added acid-soluble forms such as rock phosphate are gradually dissolved and also increase the adsorbed forms. Above a pH of 6 the trend is just the opposite. Soluble and adsorbed forms tend to change to acid-soluble forms, whereas added acid-soluble forms such as rock phosphate do not change. A pH of 6 is therefore a critical pH in these soils.⁶

The relative availability to crops of these different forms may change as the nature of the soil colloids varies in different sections of the country. As far as the corn belt is concerned, the methods described below have given excellent correlations between chemical value and crop response to added phosphate.⁶

Extracting solutions

The only important difference between methods for determining available forms of soil nutrients and the usual quantitative methods for any particular element lies in the extracting solution. This must dissolve and remove only those forms of the nutrient of immediate significance to plant growth and must do so with the required quantitateness. There is little to be gained by applying quantitative methods for phosphorus or any other nutrient to a soil extract when the extracting solution has not removed the correct forms of the nutrient quantitatively or at least in amounts proportional to the total present.

Method 1 for adsorbed phosphorus and method 2 for the combined forms, described under "Quick-test technics," were devised as rapid methods for practical use.⁷ They do not remove all of each form in the time allowed. Instead, they probably remove proportional parts of each, and in addition, the results are more strongly influenced by the more readily soluble portion of each form. Method 3 and 4, described under "Laboratory technics," were devised for the quantitative estimation of each group of forms separately (2). Method 3 extracts the adsorbed forms. Method 4 extracts both, and the acid-soluble forms are calculated by difference. Method 2 gives the best correlation between the value obtained and crop response to added phosphates for the usual corn belt crops. This means that the sum of the adsorbed and acid-soluble forms is the measure of phosphate effectiveness for these crops. This method is now the standard laboratory and quick-test method at the Illinois station and

⁵ Bray, R. H., and Dickman, S. R. 1942 Fluoride extraction methods for soil phosphorus. Ill. Agr. Exp. Sta. Mimeo. Leaflet AG 1006.

⁶ Bray, R. H. Unpublished data, 1944.

⁷ Bray, R. H. 1942 Rapid tests for measuring and differentiating between the adsorbed and acid-soluble forms of phosphates in soils. Ill. Agr. Exp. Sta. Mimeo. Leaflet AG 1028.

gives a somewhat better correlation with crop response than does method 4, the more quantitative method.

In the foregoing discussion the term "available forms" is restricted to those which are of most immediate significance to crop growth and whose variations in amount are responsible for variations in crop growth and response to added phosphates. It is not implied that the phosphorus not measured is making absolutely no contribution to crop growth.

The following methods will need to be modified if appreciable arsenic or amounts of iron much over 15 p.p.m. are extracted. In such cases the reduction method under "Total phosphorus," may have an application.

Quick-test technics

Method 1. Adsorbed phosphorus.

Reagents

- (g) *Ammonium fluoride stock solution* (approximately N NH_4F). Dilute 37 gm. of NH_4F to 1,000 ml. with distilled water. Keep in wax-lined bottle.
- (h) *Approximately 0.5 N HCl*. Dilute 20.2 ml. of concentrated HCl up to 500 ml. with distilled water.
- (i) *Adsorbed phosphorus extracting solution*. Add 15 ml. of N NH_4F and 25 ml. of 0.5 N HCl to 460 ml. of distilled water. This gives a solution 0.03 N in NH_4F and 0.025 N in HCl. It will keep in glass more than 1 year.
- (j) *Concentrated molybdate reagent*. Dissolve 100 gm. of chemically pure ammonium molybdate in 850 ml. of distilled water. Filter and cool. Make a second solution of 1,700 ml. of concentrated hydrochloric acid (36 per cent) mixed with 160 ml. of water. Cool. Add the first solution slowly to the second solution, stirring constantly. This reagent will keep 3 to 4 years.
- (k) *Tin rod*.
- (l) *Standard phosphate solution*. A solution containing 100 γ of P per ml. (100 p.p.m. of P) made as directed in (c) under "Total phosphorus."

Directions:

Weigh or measure 1 gm. of air-dried soil into a flat-bottomed glass vial, (15 $\frac{1}{2}$ by 50 mm. is a convenient size), and add 7 ml. of the extracting solution (i). Stopper and shake for 1 minute and allow to settle until the supernatant solution is clear. Then add 0.30 ml. of the concentrated molybdate reagent (j) and stir with the tin rod until maximum color develops. The tin rod should be kept bright for rapid development. The colors obtained can be compared with standard phosphate solutions (l), containing 0.6, 1.7, 2.8, and 4.5 p.p.m. of phosphorus, which are developed in the same sized tubes in the same way. The extracting solution for this method is so dilute that settling is not rapid. Filtration before color development may be preferred by some. For each milliliter of filtrate taken, add 0.05 ml. of molybdate (j) and stir with the tin rod. When a large number of tests are being run it is quicker to use stannous chloride reagent. When this is used make it up to twice the strength described below (p), and add 0.6 ml. to the supernatant solution in each vial or in proportional amounts where filtration is practiced. A color comparator may be used, but the colors developed are usually too deep for the photoelectric photometer (see method 1A).

Method 2. Acid-soluble and adsorbed phosphorus.

Reagents:

- (g, h, j, k, and l) under method 1, and in addition
- (m) *Acid-soluble and adsorbed extracting solutions*. Add 15 ml. of N NH_4F (g) and 100 ml. of 0.5 N HCl (h) to 385 ml. of distilled water. This gives a solution 0.03 N in NH_4F and 0.1 N in HCl. It will keep in glass more than 1 year.

Directions:

Weigh or measure 1 gm. of air-dried soil into a flat-bottomed vial (about 15½ by 50 mm.), and add 7 ml. of extracting reagent (m). Stopper and shake for 40 seconds. Allow to settle until supernatant solution is clear; then develop and read as described under method 1. Settling is more rapid with this method.

*Laboratory techniques***Method 1A. Adsorbed phosphorus.**

Reagents [as described by Dickman and Bray (7)]:

(i) under method 1, and in addition

(n) *Stannous chloride, stock solution.* Dissolve 10 gm. of reagent grade stannous chloride dihydrate in 25 ml. of concentrated hydrochloric acid. This solution should be kept in a black glass-stoppered bottle and prepared fresh every 6 weeks.

(o) *Ammonium molybdate-hydrochloric acid.* Dissolve 15 gm. of reagent grade ammonium molybdate in about 350 ml. of distilled water. Add 350 ml. of 10 N HCl slowly with stirring. Cool to room temperature and dilute to 1,000 ml. with distilled water. Mix well and store in a black glass-stoppered bottle. Prepare fresh every 2 months.

(p) *Stannous chloride, dilute reagent.* Add 1 ml. of stannous chloride, stock (n) to ¼ liter of distilled water. Mix. Make fresh every 4 hours as needed.

Directions:

Weigh 1 gm. of air-dried soil into a glass vial; add 7 ml. of adsorbed phosphorus extracting solution (i) and shake for 1 minute.

Pour immediately on a 7-cm. filter paper. To 1 ml. of the filtrate, add 6 ml. of distilled water and 2 ml. of ammonium molybdate-hydrochloric acid reagent (o). Mix well. Add 1 ml. of stannous chloride, dilute reagent (p). Mix well. After 5 or 6 minutes read in a photoelectric photometer standardized against similarly developed standard phosphate solutions made up in reagent (i) from reagent (l).

Method 2A. Acid-soluble and adsorbed phosphorus.**Reagents:**

(m, o, and p)

Directions:

Weigh 1 gm. of air-dried soil into a glass vial; add 7 ml. of the acid-soluble and adsorbed extracting solution (m), and shake for 40 seconds. Pour immediately on a 7-cm. filter paper and proceed to develop the color as directed under method 1A.

Method 3. Total adsorbed phosphorus.**Reagents:**

(o and p), and in addition

(q) *Approximately 0.5 N ammonium fluoride.* Dissolve 18.5 gm. of solid NH_4F in 1 liter of distilled water. Adjust to pH 7. Store in a wax-lined bottle.

(r) *Boric acid solution (approximately 0.8 M).* Dissolve approximately 50 gm. of reagent grade boric acid in 1 liter of warm distilled water [as described by Kurtz (9)].

Directions:

Shake 1 gm. of NH_4 -saturated soil for 1 hour in 50 ml. of 0.5 N ammonium fluoride (q). Filter the suspension on a 4.25-cm. Büchner funnel. Pipette an aliquot* (usually 10 ml.) of the clear filtrate† into a 25 by 200-mm. Pyrex tube graduated at 35 ml. Add 15 ml. of

* Phosphorus in this solution should be determined soon after extraction is made.

† The filtrates may be colored by organic matter which has been extracted by the fluoride. This color does not ordinarily interfere with the photometer reading which is made at 675 mμ. In highly organic soils, interferences are handled by reading the undeveloped solutions. In extreme cases, it may be desirable to flocculate the organic matter in the aliquot with HCl and filter.

approximately 0.8 *M* H_3BO_3 (r), and then add water to make the volume exactly 35 ml. Add 10 ml. of the ammonium molybdate-HCl reagent (o) and mix by inverting the tube three times. Follow immediately with 5 ml. of stannous chloride, dilute reagent (p) and mix again. After 5 or 6 minutes read in a photoelectric photometer.

Method 4. Total acid-soluble and adsorbed phosphorus.

Reagents:

(o, p, and r) and in addition

(s) 0.1 *N* hydrochloric acid. Make approximately 8.1 ml. of concentrated HCl up to 1,000 ml. with distilled water.

(t) Solid ammonium fluoride.

Directions:

Shake 1 gm. of air-dried soil with 50 ml. of 0.1 *N* HCl (s) for 30 minutes. Add 1.0 gm. of solid NH_4F (t), which makes the solution approximately 0.5 *N* in fluoride, and shake for an additional 60 minutes. Filter with suction on a Büchner funnel. Take an aliquot of the filtrate, add 15 ml. of 0.8 *M* H_3BO_3 , and proceed as directed under method 3.

ORGANIC PHOSPHORUS

The organic forms of phosphorus are of importance in fertility because they are, in general, an indirect source of the soluble forms. Phosphates, as well as nitrates, are produced when soil organic matter is decomposed. After liberation, soil reactions sooner or later make the phosphates a part of the adsorbed and acid-soluble forms. Thus, they help counterbalance the effect of crop removal, and in highly organic soils a good level of the available forms is often maintained over a period of years, despite crop removals. But it is the level of the available forms already present, not the amount liberated from the organic matter during the growing season, which appears to determine the fertility of the soil for that season as far as phosphorus is concerned.

The following method is essentially the one described by Dickman and DeTurk (5), modified by using the fluoride extraction method for the removal of the phosphate released from the organic matter. The difference between the amount of phosphorus removed by method 4 after peroxide treatment and the amount removed by method 4 before peroxide treatment is the measure of the organic phosphorus.

Reagents

(h, o, p, r, s, and t) and in addition

(u) *Phosphorus-free hydrogen peroxide*. A solution of 30 per cent hydrogen peroxide is treated to remove phosphorus by one of the procedures described by Dickman and Bray (6) or Dickman and DeTurk (5).

Directions

Weigh a 1-gm. sample of 35-mesh soil into a large test tube graduated at 50 ml. Add hydrogen peroxide, equivalent to approximately 15 ml. of 30 per cent strength, and 10 ml. of water. Mix thoroughly and place on a slow steam bath for $\frac{1}{2}$ hour. Add 15 ml. of water, 10 ml. of 0.5 *N* HCl (h), and finally make up to 50 ml. with water. Stopper the tube, place in a shaker, and shake for 30 minutes. Add 1 gm. of ammonium fluoride (t); shake for an additional hour, and filter on a Büchner funnel with suction.

To a suitable aliquot (5 to 10 ml.) in a 250-ml. beaker, add 15 ml. of 0.8 *M* boric acid (r), and evaporate to dryness. Add 10 ml. of approximately 0.1 *N* HCl and re-evaporate.

Take up the residue with small portions of 0.1 N HCl and determine the phosphate in the aliquot according to the procedure described under method 4 above for acid-soluble and adsorbed phosphates.

The organic phosphorus is taken as the difference between the phosphorus removed by this procedure and that removed from duplicate samples when extracted by method 4.

REFERENCES

- (1) BEAR, F. E., AND TOTH, S. J. 1942 Phosphate fixation in soil and its practical control. *Indus. and Engin. Chem., Analyt. Ed.* 34: 49.
- (2) BRAY, R. H., AND DICKMAN, S. R. 1941 Adsorbed phosphates in soils and their relation to crop responses. *Proc. Soil Sci. Soc. Amer.* 6: 312.
- (3) BURD, J. S., AND MURPHY, H. F. 1939 The use of chemical data in the prognosis of phosphate deficiency in soils. *Hilgardia* 12: 323.
- (4) DAVIS, L. E. 1935 Sorption of phosphates by non-calcareous Hawaiian soils. *Soil Sci.* 40: 129-158.
- (5) DICKMAN, S. R., AND DeTURK, E. E. 1938 A method for the determination of the organic phosphorus of soils. *Soil Sci.* 45: 29-39.
- (6) DICKMAN, S. R., AND BRAY, R. H. 1940 Removal of phosphates from solutions of hydrogen peroxide. *Indus. and Engin. Chem., Analyt. Ed.* 12: 279.
- (7) DICKMAN, S. R., AND BRAY, R. H. 1940 Colorimetric determination of phosphate. *Indus. and Engin. Chem., Analyt. Ed.* 12: 665.
- (8) DICKMAN, S. R., AND BRAY, R. H. 1941 Replacement of adsorbed phosphate from kaolinite by fluoride. *Soil Sci.* 52: 263-273.
- (9) KURTZ, L. T. 1942 Elimination of fluoride interference in the molybdenum blue reaction. *Indus. and Engin. Chem., Analyt. Ed.* 14: 855.
- (10) RUSSELL, J. R., AND PRESCOTT, J. A. 1916 The reaction between dilute acids and the phosphorus compounds of the soil. *Jour. Agr. Sci.* 8: 65.
- (11) SCARSETH, G. D. 1935 The mechanism of phosphate retention by natural aluminosilicate colloids. *Jour. Amer. Soc. Agron* 27: 596.
- (12) SCHRICKER, J. A., AND DAWSON, P. R. 1939 Improved molybdenum blue reagents for determination of phosphorus and arsenic. *Jour. Assoc. Off. Agr. Chem.* 22: 167.
- (13) SHERMAN, M. S. 1942 Colorimetric determination of phosphorus in soils. *Indus. and Engin. Chem., Analyt. Ed.* 14: 182.
- (14) STEELE, J. G. 1935 Abstract of Doctor's Dissertation 15. Ohio State University Press, Columbus.
- (15) STOUT, P. R. 1939 Alterations in the crystal structure of clay minerals as a result of phosphate fixation. *Proc. Soil Sci. Soc. Amer.* 4: 177.

DETERMINATION OF TOTAL NITROGEN, AMMONIA, NITRATES, AND NITRITES IN SOILS¹

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TOTAL NITROGEN

The Kjeldahl method has long been the standard procedure for determining total nitrogen. Various modifications for increasing the rapidity or simplicity of the determination have been introduced from time to time, but the fundamental principles still apply. The organic matter in the sample is oxidized by boiling with concentrated H_2SO_4 in connection with a catalyst, or a salt that has been added to raise the boiling point of the mixture, or both, to speed the reaction. Organic nitrogen is converted to ammonia and fixed in the digestion solution as ammonium sulfate. The ammonia is released from this solution by the addition of excess alkali and is distilled over into an excess of standard acid. The excess standard acid is titrated with a standard alkaline solution, using a suitable indicator. If mercury is used as the catalyst, it must be precipitated with potassium sulfide prior to distillation, otherwise a mercurammonium compound will be formed, which fails to release ammonia on the addition of the alkali.

Metallic mercury, mercuric oxide, copper sulfate, and anhydrous sodium sulfate, used separately and in various combinations, have long been the standard materials that are used for hastening the digestion process, and these have not been greatly improved upon. More recently, considerable work has been done with metallic selenium and selenium oxychloride (4, 7, 9), which oxidize organic matter very rapidly but which, when used without mercury and boiled vigorously, may cause a loss of nitrogen. Furthermore, the rapid clearing of the digestion solution as a result of their use often falsely leads the analyst into believing that all the nitrogen has been converted into the mineral form, with the result that the digestion is stopped prematurely. A mixture of metallic mercury (0.65 gm.) and selenium (0.2 gm.) or selenium oxychloride alone (1 ml. of a solution containing 2.5 ml. selenium oxychloride per 500 ml. of concentrated H_2SO_4) has proved very satisfactory, provided the digestion is carried beyond the point of clearing (approximately 15 minutes). With soils, the total digestion period should be 1 hour (7, 9). This procedure results in about 25 per cent saving of time for most materials, at only a slight increase in the expense of the operation.

The ferric sulfate method (10, 13) employs 10 gm. anhydrous dipotassium phosphate, 6 gm. ferric sulfate, and 0.65 gm. mercury, with a 30-minute digestion at full heat of the gas flame. By this method rapid oxidization is effected, and the results have been good, but the large amount of salts used in the process

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are cumbersome to deal with, too much individual attention being required for acceptance of the procedure in a routine laboratory.

A recent method (8) using perchloric acid (0.5 ml. of a 35 per cent grade), after a preliminary 10-minute vigorous boiling with concentrated H_2SO_4 and selenium oxychloride, reduces the digestion time to about 30 minutes, but the technique of heating requires careful attention. Results on soils with this method tend to run slightly low.

The correct determination of nitrogen is not so simple and straightforward as is usually thought, and faulty technique may easily lead to erroneous results. In applying the Kjeldahl method to soils, a comparatively large sample is used (10 gm. for average soils and 5 gm. for soils high in organic matter). Consequently, the sample must be finely pulverized to prevent bumping during the digestion process, especially if the distillation is to be carried out in the same flask without separation from the soil. Grinding the soil sample in a ball mill to an impalpable powder, or at least until it will pass a 0.5-mm. sieve, is essential. The amount of nitrate nitrogen in soils is negligible in comparison with that of the organic nitrogen and may be disregarded, especially since most of it is reduced to ammonia by the organic matter during the period of digestion.

Procedure

Digest 10 gm. of soil in a 500-ml. Kjeldahl flask with 30 ml. concentrated H_2SO_4 , 0.7 gm. HgO (or 0.65 gm. Hg), and 5-10 gm. anhydrous Na_2SO_4 . Continue the digestion for 1½-2 hours. After cooling, add about 200 ml. distilled H_2O . When cold, add a pinch of zinc dust and an excess (about 100 ml.) of approximately 45 per cent NaOH solution containing about 12 gm. K_2S per liter. Join the flask to the condenser by means of a Kjeldahl connecting bulb, taking care that the tip of the condenser tube extends below the surface of the standard acid in the receiving flask. Mix the contents of the Kjeldahl flask by shaking, and collect about 150 ml. of distillate. Titrate the excess acid¹ in the receiving flask with 0.01 *N* alkali, using methyl red as the indicator if NaOH is used, alizarin if NH_4OH is the standard alkaline solution, or a mixed indicator. Run a blank determination in exactly the same manner, but using about 0.2 gm. sucrose in place of the soil, to correct for any nitrogen contained in the reagents.

The percentage of nitrogen in the soil on the basis of a 10-gm. sample = $(B-T) \times N \times 0.14$, where B = blank titration in milliliters of standard alkali, T = actual titration in milliliters of standard alkali, and N = normality of the standard alkali.

AMMONIA

Ammonia is difficult to determine directly in soils because of the danger of hydrolyzing nitrogenous compounds during the process. Furthermore, it is

¹ If desired, the ammonia may be distilled into 25-50 ml. of 4 per cent boric acid (11) (50 ml. boric acid takes care of 95 mgm. of nitrogen as NH_3) and then titrated with either 0.1 *N* HCl or 0.1 *N* H_2SO_4 , using 4 drops of the following mixed indicator:

Mixed indicator. Mix 10 ml. of 0.1 per cent bromocresol green in 95 per cent alcohol with 2 ml. of 0.1 per cent methyl red in 95 per cent alcohol. The color produced by this indicator in boric acid is bluish purple. With a trace of ammonia the color becomes bluish green. Titrate with standard acid until the blue color just disappears. One drop in excess will turn the solution pink. If titrated to a faint pink, subtract 0.02 ml. from the reading. With this procedure, only one standard solution is necessary.

rapidly oxidized to nitrite and nitrate under conditions of warm, moist storage. Valid determinations of all these constituents can be made, therefore, only on soil samples immediately after they have been taken. Such samples may be dried rapidly in an oven at 55° C. Unlike the nitrite and nitrate, ammonia is present in the soil as an exchangeable ion that is adsorptively bound to the cation-exchange complex. It must, therefore, be replaced by an excess of some other cation for quantitative determination.

Ammonia may be accurately determined at ordinary temperatures by aerating a suspension of the soil with a 4 per cent solution of K_2CO_3 and a 20 per cent solution of KCl in a specially designed apparatus, but the method is long and tedious (6).

Most analysts employ salts to replace the ammonia held in the soil (2, 5). Various strengths of potassium chloride or sodium chloride solutions have been used, with or without HCl to pH 1.0–1.5, the soil being either leached or shaken with these mixtures. Aliquots are then distilled with excess MgO and the ammonia is caught in 0.02 *N* acid, the excess acid being titrated back with 0.02 *N* NaOH. Other workers prefer to nesslerize the distillate if the amount of ammonia is less than 2 mgm.

Procedure (5)

Place 25 gm. soil in a 400-ml. beaker. Add 100 ml. of a cold solution of *N* NaCl. Stir well and let stand for $\frac{1}{2}$ hour. Decant the liquid through an 18.5-cm. Whatman No. 44 filter. Wash the soil with normal sodium chloride solution once by decantation and then transfer it completely to the filter. Continue the leaching until the volume of the filtrate approximates 500 ml. Add excess MgO (3–4 gm.) and then distill the filtrate into a measured volume (10–15 ml.) of 0.02 *N* HCl. Add a small piece of paraffin to the distillation flask to prevent frothing. Collect about 150 ml. of distillate, and titrate the excess acid with 0.02 *N* NaOH, using either methyl red or bromocresol green indicator. If the latter indicator is used, the end point is reached when the color of the indicator matches that in a reference buffer solution of pH 4.7–4.8 containing the same quantity of indicator.

For soils with a high content of ammoniacal nitrogen, it is necessary to collect a second half-liter of leachate, or to leach with a more concentrated (15 per cent) solution of sodium chloride.

NITRATES

Nitrates and nitrites are readily soluble in water and are not adsorbed by the soil complex. Nitrates may be determined in the soil extract either by reducing them to ammonia with Devarda's alloy and then distilling off the ammonia, or by a colorimetric procedure, using phenoldisulfonic acid.

In the reduction method (14) the soil extract is distilled very slowly with 2 gm. Devarda's alloy and 5 ml. of a 42 per cent solution of NaOH, using a special trap or such other precautions as may be necessary to hold back the spray that is formed. The ammonia is collected in 10–35 ml. of 0.02 *N* HCl, and the excess acid is titrated with 0.02 *N* NaOH, using methyl red or bromocresol green indicator.

The phenoldisulfonic-acid method (1, 3, 14) has been used for over 30 years and is still the most popular one, but a number of precautions are necessary to eliminate certain interfering substances. In this method the nitrate nitrogen

is fixed as nitrophenoldisulfonic acid. Addition of NH_4OH produces a yellow color by the formation of ammonium nitrophenoldisulfonic acid. The intensity of the color is proportional to the amount of nitrate nitrogen present.

Reagents

Phenoldisulfonic acid. Dissolve 25 gm. pure white phenol in 150 ml. concentrated H_2SO_4 . Add 75 ml. fuming H_2SO_4 (13–15 per cent SO_3), and heat at 100° for 2 hours.

Standard nitrate solution. Dissolve 0.72 gm. pure recrystallized KNO_3 and dilute to 1 liter with distilled water. Evaporate 10 ml. of this solution in a porcelain evaporating dish on a steam bath. Moisten the residue quickly and thoroughly with 2 ml. phenoldisulfonic acid, stir with a flattened glass rod to insure intimate contact, and dilute to 1 liter. One milliliter equals 0.001 mgm. N.

Determination

Weigh 100 gm. air-dry soil into a 500-ml. Erlenmeyer flask. Add 2–4 gm. of pulverized quicklime (CaO) and 200 ml. distilled H_2O . Close the flask with a rubber stopper. Shake 3–5 minutes, allow to stand 20 minutes, and filter. Pour back or reject the filtrate until it comes through clear. Place 50 ml. of the filtrate in a porcelain evaporating dish and evaporate just to dryness on the steam bath. When cool, moisten the residue quickly and thoroughly with 2 ml. phenoldisulfonic acid. Rub the sides of the dish with a flat stirring rod and allow to stand about 10 minutes. Dilute with 10–20 ml. distilled H_2O and then add excess NH_4OH until the yellow color is fully developed. After cooling, filter, if necessary, and make up to 50 ml. with distilled H_2O . Compare in a colorimeter with a standard prepared by taking 10 ml. of the standard nitrate solution, making alkaline with NH_4OH , and diluting to 50 ml. This solution contains 0.01 mgm. N or 0.2 p.p.m. N. If the color of the unknown is too intense for the standard, make the proper dilutions. In lieu of the colorimeter, an electric photometer, with a blue filter, may be used. Nitrate curves should be prepared previously by plotting the percentage of transmission against the parts per million of nitrate nitrogen. A blank determination should be run on all reagents.

Precautions

If the soil contains more than 15 p.p.m. chlorides, silver sulfate must be added to the soil suspension, before shaking, to precipitate the chlorides (10 ml. of a 0.4 per cent solution will take care of 80 p.p.m. chlorides.)

In some soils, the amount of organic matter imparts a color to the extract, which seriously interferes with the determination. In such cases, add 5–10 drops nitrate-free superoxol¹ during the evaporation of the aliquot. Repeat the superoxol treatment if necessary, but a blank determination is especially necessary when this reagent is used.

If nitrites are present in concentrations greater than 1 p.p.m., they should be corrected for, otherwise high values will be obtained for nitrate nitrogen.

NITRITES

Nitrites are seldom present in soils in amounts sufficient to warrant their determination. In most soils they are rapidly oxidized to nitrates, and it is doubtful whether reliable values can be obtained even when the determination is carried out immediately after the sample is collected. Furthermore, it is very difficult to prepare a clear, colorless soil extract for this determination without change in nitrite content.

¹ For purification see *Indus. and Engin. Chem., Analyt. Ed.* 16: 181. 1944.

In special cases, where this determination is necessary, the standard procedure, using sulfanilic acid and alpha-naphthylamine, may be employed, using a water extract of the soil prepared as under the nitrate determination (1).

Reagents

Sulfanilic acid. Dissolve 1.6 gm. sulfanilic acid in 200 ml. dilute acetic acid (29 per cent). Heat gently to dissolve. Keep in a glass-stoppered bottle.

Naphthylamine acetate. Dissolve 0.5 gm. alpha-naphthylamine in 100 ml. dilute acetic acid (29 per cent). Heat gently to dissolve. Keep in a brown glass-stoppered bottle. Prepare fresh supply every 2 or 3 days.

Silver nitrite. Dissolve 10 gm. AgNO_3 in 20 ml. hot distilled H_2O . Dissolve 10 gm. NaNO_2 in 15 ml. distilled H_2O , and heat. Mix these solutions while hot, and stir. Filter and wash 10 times with ice-cold H_2O . Place precipitate and filter paper between white blotting paper and press it gently to squeeze out the moisture. Wrap it with another filter paper and dry in a desiccator in a dark place for a week or longer.

Standard sodium nitrite solution. *Solution A*—Dissolve 0.55 gm. AgNO_2 in 50 ml. distilled H_2O in a beaker by heating. In another beaker dissolve 0.3 gm. NaCl in 25 ml. H_2O . Add the NaCl solution to the AgNO_2 solution, and stir. Cool, filter into a 500-ml. volumetric flask, and wash about 15 times. Add 1 ml. chloroform, make up to mark, and preserve in a brown bottle in a dark place. One milliliter contains 0.1 mgm. nitrous N. *Solution B*—Dilute 10 ml. of solution A to 1 liter, and keep in a brown bottle. One milliliter contains 0.001 mgm. nitrous N.

Standard colored solution. Transfer 10 ml. solution B to a 100-ml. flask, add 75 ml. H_2O and 2 ml. each of the sulfanilic acid reagent and the alpha-naphthylamine acetate. Shake, make up to the mark, and shake again thoroughly. Set aside for 15–20 minutes, and compare with the unknown in the colorimeter. One milliliter of this pink standard solution (C) contains 0.0001 mgm. nitrous nitrogen.

Determination

Obtain a water extract of the soil as under the nitrate determination. Take a suitable aliquot, depending upon the amount of nitrite N present. Dilute to about 95 ml. and add 2 ml. each of the sulfanilic acid and alpha-naphthylamine acetate. Make up to the mark, shake thoroughly, and set aside for 15–20 minutes. Compare with the standard (C) in a colorimeter.

More recently, the use of sulfanilamide and *N* (1-naphthyl)-ethylenediamine dihydrochloride has been proposed (12). These reagents were found superior to the sulfanilic acid and alpha-naphthylamine in that the color developed is clearer, reaches its maximum intensity more rapidly, and remains stable for a longer time. A standardized solution of sulfanilamide is substituted for sodium nitrite as the primary standard to obviate the difficulties arising from the instability of the latter.

REFERENCES

- (1) FRAPS, G. S., AND STERGES, A. J. 1931 Estimation of nitric and nitrous nitrogen in soils. *Tex. Agr. Exp. Sta. Bul.* 439.
- (2) HARPER, H. J. 1924 The determination of ammonia in soils. *Soil Sci.* 18: 409–418.
- (3) HARPER, H. J. 1924 The accurate determination of nitrates in soils. *Indus. and Engin. Chem.* 16: 180–183.
- (4) LAURO, M. F. 1931 Use of selenium as catalyst in determination of nitrogen by Kjeldahl method. *Indus. and Engin. Chem., Analyt. Ed.* 3: 401–402.
- (5) McLEAN, W., AND ROBINSON, G. W. 1924 A new method for the determination of ammoniacal nitrogen in soils. *Jour. Agr. Sci.* 14: 548–554.
- (6) MATHEWS, D. J. 1920 The determination of ammonia in soil. *Jour. Agr. Sci.* 10: 72–85.

- (7) OSBORN, R. A., AND KRASNITZ, A. 1933 A study of the Kjeldahl method: II. Comparison of selenium with mercury and with copper catalysts. *Jour. Assoc. Off. Agr. Chem.* 16: 110-113.
- (8) PEPKOWITZ, L. P., PRINCE, A. L., AND BEAR, F. E. 1942 A rapid Kjeldahl digestion method using perchloric acid. *Indus. and Engin. Chem., Analyt. Ed.* 14: 856-857.
- (9) PRINCE, A. L. 1934 Report on nitrogen. *Jour. Assoc. Off. Agr. Chem.* 17: 246-250.
- (10) PRINCE, A. L. 1941, 1943 Report on nitrogen. *Jour. Assoc. Off. Agr. Chem.* 24: 264-268 (1941); 26: 54-59 (1943).
- (11) SCALES, F. M., AND HARRISON, A. P. 1920 Boric acid modification of the Kjeldahl method for crop and soil analysis. *Indus. and Engin. Chem.* 12: 350-352.
- (12) SHINN, M. B. 1941 Colorimetric method for determination of nitrite. *Indus. and Engin. Chem., Analyt. Ed.* 13: 33-35.
- (13) STUBBEFIELD, F. M., AND DETURK, E. E. 1940 Effect of ferric sulfate in shortening Kjeldahl digestion. *Indus. and Engin. Chem., Analyt. Ed.* 12: 396-399.
- (14) WRIGHT, C. H. 1939 Soil Analysis: A Handbook of Physical and Chemical Methods, ed. 2. Thomas Murby and Co., London.

DETERMINATION OF SOIL ORGANIC MATTER

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Organic matter is a constituent highly variable with respect to the quantity in a soil and the chemical composition. Its importance in affecting the physical and chemical characteristics and the productivity of a soil needs no extended discussion to account for the continued interest in the determination. Good reviews of methods, with many references to the extensive literature, have been published by Waksman and Stevens (11) and by Alexander and Byers (1). As pointed out by the latter authors, Sprengel in 1826 published the statement that soil organic matter averages close to 58 per cent in content of carbon. This figure is still accepted as the best average for an admittedly inconstant value, and is the basis of the conventional factors 1.724 and 0.471 by which percentages carbon and carbon dioxide, respectively, found on analysis, are multiplied to obtain an assumed percentage of organic matter. These factors, of course, refer to the carbon contained in or the carbon dioxide derived from the organic matter in the soil; that attributable to inorganic sources such as carbonates or elemental carbon (graphite, coke in cinders, coal, or charcoal) is to be deducted. The former can be determined with high accuracy, but the latter cannot. Fortunately, an error from the presence of elemental carbon is usually so small that it is negligible; if sufficient to be of importance, that fact should become apparent on close examination of the soil under the microscope.

The imperfections of the numerous methods that have been used as a measure of organic matter in soils, from simple loss on ignition to low temperature treatment with various solvent or oxidizing solutions, have likewise been pointed out by Alexander and Byers. These authors conclude that a determination of total carbon with correction for that from inorganic sources and calculation based on the factors mentioned is the most reliable method yet proposed. The determination of total carbon by combustion in oxygen is accurate and reasonably rapid (3), but the necessity for special apparatus and accessories has led to the substitution of various procedures of wet combustion, generally with hot concentrated sulfuric and phosphoric acids and chromic anhydride or other oxidizing agents, for the combustion furnace and oxygen supply. It has been reported that oxidation of organic carbon to carbon dioxide may be incomplete with the wet combustion procedure, with formation of volatile organic compounds such as acetic acid or carbon monoxide (4, 7). The writer has had experience with a method of this class as applied to soil (8). Later work indicated that the good results obtained were largely attributable to the empirical standardization of the titrating solution against a similar sample of known organic carbon content as determined by furnace combustion. That the wet oxidation had probably been incomplete was shown by the fact that more nearly theoretical values were obtained when the gases aerated from the boiling oxidizing mixture were passed over heated copper oxide prior to absorption.

It has been asserted, however, that by the use of an improved oxidizing mixture the conversion of organic carbon to carbon dioxide can be made quantitative (6).

In view of the indefinite composition of soil organic matter, it seems unnecessary to base its estimation on a highly precise determination of organic carbon. A simpler and more rapid method, although less exact should serve the purpose quite as well in many instances. Such a method has been proposed (9, 10) and numerous modifications, all on similar principles, have appeared since. A study of several such reduction methods, as compared with furnace combustion data for organic carbon in a series of varied soil samples from many sources and carried out by numerous collaborators, has been published by Crowther (5), with the conclusion that these methods may serve a useful purpose. Using the same series of samples, the writer compared the original method, with some changes hereinafter described, with the Walkley-Black procedure (12), perhaps the simplest that has been proposed, and a variation of the latter that seemed logical in the light of available knowledge of the reactions concerned. In this comparison, the values for blank titrations, supposed to be applicable to a sample containing no organic carbon, were determined by carrying through the procedures with similar soil samples that had been ignited in oxygen to burn off all the carbon. The object was to allow for the error from thermal decomposition of chromic acid in sulfuric acid, which has been shown to be positively catalyzed by the inorganic constituents of soils. The three methods compared are outlined:

- (a) Schollenberger method with changes, described hereinafter.
- (b) Walkley-Black method. To the sample in a 250-ml. Erlenmeyer flask add 10 ml. *N* potassium dichromate and 20 ml. concentrated sulfuric acid, and continue stirring for 1 minute. The heat of dilution of the acid is depended upon to carry the reaction to completion. Dilute further, cool, and proceed with the determination in the same flask, as in *a*.
- (c) Walkley-Black method, modified. Proceed as in *b*, but add only 10 ml. concentrated sulfuric acid; insert a thermometer at once and heat to 140° C. and maintain that temperature with stirring for 5 minutes. Dilute and cool, and proceed further as in *b*.

With the theoretical carbon value of the 0.2 *N* titrating solution, and the furnace combustion data for organic carbon in the samples as bases for calculation, the ranges of the indicated recovery ratios by these methods were 0.860–0.958 for method *a*, 0.698–0.860 for *b*, and 0.765–0.886 for *c*. The average recovery ratios with standard deviations were $0.904 \pm .013$ for *a*, $0.790 \pm .019$ for *b*, and $0.812 \pm .015$ for *c*. Since the recovery was highest and the standard deviation lowest with method *a*, it may be concluded that this procedure was the best. Allison (2) came to the same conclusion in a similar study. He found that the variation to be expected between duplicate determinations by the dichromate reduction method, substantially as originally described, is less than that to be expected from duplicate samplings; hence, for the practical estimation of organic matter in soil, this rapid method should be as good as the most accurate combustion method. It has the advantages of requiring no correction for carbonates and of making but an incomplete attack on inorganic

carbon in coal cinders; consequently, there is less error in case these are present. But it must be noted that in the indication for organic carbon by this method, chloride in a soil sample will cause a corresponding plus error from consumption of chromic acid by forming volatile chromyl chloride, CrO_2Cl_2 , a dark-red liquid boiling at 118°C . The obvious solution for this difficulty is to remove the chloride first by washing the soil sample. Or, if the washing is objectionable because it causes some loss of water-soluble organic matter, a correction based on the chloride content may be applied, as the consumption of chromic acid by chloride has been shown to be nearly stoichiometric (5). Two gram atoms of chlorine correspond to 0.75 gm. atom of carbon, i.e., 1 part of chlorine in the sample will cause an apparent excess of approximately 0.25 part of organic matter.

Procedure. To a clean and dry 8- by 1-inch Pyrex test tube transfer 0.1961 gm. powdered pure potassium dichromate and the sample, 0.5 gm. or less if high in organic matter. Samples containing chloride in appreciable amount should first be washed on a thin pad of ignited asbestos in a Shimer filter, and the moist asbestos and soil transferred to the test tube. Mix the sample and the dichromate and wash down with 10 ml. concentrated sulfuric acid. Have ready a bath made by heating to $205\text{--}210^\circ\text{C}$. 100 ml. concentrated sulfuric acid in a wide-mouth 250-ml. Pyrex flask. Stir the contents of the test tube with a thermometer, pushing down any charred particles, and immerse the tube in the bath until the temperature of the contents reaches 175°C ., in $1\frac{1}{2}\text{--}2$ minutes. Remove and continue stirring for 1 minute, then cool in water. Pour the mixture into 50 ml. cold water in a 250-ml. beaker and add rinsings to recover all the residual chromic acid in 100 ml. total volume. Stir into the cold solution about 5 gm. powdered sodium fluoride—a level teaspoonful—and add two or three drops of a 0.5 per cent solution of diphenylamine in concentrated sulfuric acid. Titrate with 0.2 *N* ferrous ammonium sulfate until the brilliant blue color, which usually does not appear until the titration is started, fades to a muddy green with only a suggestion of blue. This end point is very sharp. If less than half of the dichromate added is indicated by the titration to remain, it is advisable to repeat the determination with a smaller sample. Run a blank with a similar soil sample which has been thoroughly ignited to burn off all the carbon. Deduct from the titration figure with this ignited sample that obtained with the sample not ignited; the difference corresponds to chromic acid reduced by the organic matter in the sample. In theory, 1 ml. 0.2 *N* solution is equivalent to 0.0006 gm. carbon or approximately 0.0012 gm. organic matter as determined by this method with 90 per cent recovery, but it is best to standardize the titrating solution against a similar soil of known organic carbon content.

0.2 N ferrous ammonium sulfate. The salt is obtainable in fine crystals of virtually theoretical composition, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, which keep well. A solution of 19.61 gm. in water containing 5 ml. concentrated sulfuric acid, finally diluted to 250 ml., should be 0.2 *N*. The solution may be kept at full strength indefinitely under an atmosphere of hydrogen, but without this precaution it loses strength rapidly. It is best to prepare the solution as needed, and throw away any left after a day or two. The strength may be checked against pure potassium dichromate; 0.1961 gm. of the latter dissolved in 100 ml. water containing 10 ml. concentrated sulfuric acid, with 5 gm. sodium fluoride and diphenylamine indicator, should require 20.00 ml. 0.2 *N* solution in a titration.

Potassium dichromate. Crystals of reagent grade are finely powdered and dried at 110°C . and kept in a small bottle in a desiccator.

Sodium fluoride. The pure salt, sold as a powder. The purpose of its addition in this titration is to improve the characteristics of diphenylamine as an indicator; the fluoride ion forms a complex with the ferric ion and thus destroys the oxidation-reduction buffering effect in the ferric-ferrous system, with consequent sharpening of the end point. Inasmuch

as a large excess of phosphoric acid will have a similar effect, 10 ml. 85 per cent phosphoric acid may be used instead of 5 gm. sodium fluoride. The latter etches glassware severely, but otherwise is to be preferred.

Diphenylamine solution. Dissolve 0.05 gm. diphenylamine in 10 ml. concentrated sulfuric acid, and keep in a small bottle with dropper. Although diphenylamine is not an ideal indicator, it is especially adapted to this titration by its intense color and sharp change at the oxidation-reduction potential at the end point.

The foregoing procedure is recommended, but if less care has been taken in obtaining or preparing a sample, a simpler method such as the Walkley-Black may serve equally well, with proper allowance for the lower recovery ratio—that is to say, the value of the titrating solution should be established by a determination on a similar soil of known organic carbon content. As the reduction of chromic acid involves a pronounced change in color, orange to green, rapid measurements by colorimetric or photoelectric means may be substituted for titration.

REFERENCES

- (1) ALEXANDER, L. T., AND BYERS, H. G. 1932 A critical laboratory review of methods of determining organic matter and carbonates in soil. U. S. Dept. Agr. Tech. Bul. 317.
- (2) ALLISON, L. E. 1935 Organic soil carbon by reduction of chromic acid. *Soil Sci.* 40: 311-320.
- (3) BEAR, F. E., AND SALTER, R. M. 1916 Methods in soil analysis. W. Va. Agr. Exp. Sta. Bul. 159.
- (4) CHRISTENSEN, B. E., WILLIAMS, R. J., AND KING, A. E. 1937 Organic oxidation equivalent analysis: III. General method using dichromate. *Jour. Amer. Chem. Soc.* 59: 293-296.
- (5) CROWTHER, E. M., ET AL. 1935 First report of the organic carbon committee. *Trans. 3rd. Internatl. Cong. Soil Sci.* 1: 114-127.
- (6) MCCREADY, R. M., AND HASSID, W. Z. 1942 Semimicrodetermination of carbon using Van Slyke-Folch oxidation mixture. *Indus. and Engin. Chem., Analyt. Ed.* 14: 525-526.
- (7) READ, J. W., AND RIDGELL, R. H. 1922 On the use of the conventional carbon factor in estimating soil organic matter. *Soil Sci.* 13: 1-6.
- (8) SCHOLLENBERGER, C. J. 1916 Total carbon in soil by wet combustion. *Jour. Indus. and Engin. Chem.* 8: 1126.
- (9) SCHOLLENBERGER, C. J. 1927 A rapid approximate method for determining soil organic matter. *Soil Sci.* 24: 65-68.
- (10) SCHOLLENBERGER, C. J. 1931 Determination of soil organic matter. *Soil Sci.* 31: 483-486.
- (11) WAKSMAN, S. A., AND STEVENS, K. R. 1930 A critical study of the methods for determining the nature and abundance of soil organic matter. *Soil Sci.* 30: 97-116.
- (12) WALKLEY, A., AND BLACK, I. A. 1934 An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Sci.* 37: 29-38.

DETERMINATION OF CARBONATES IN SOIL

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The procedure for determining carbonates in soil as originally described (3) has been satisfactory in long-continued use, and this experience has shown the desirability of only one or two slight but important modifications in the apparatus. Carbon dioxide is liberated *in vacuo* at a comparatively low acid concentration and low temperature and in the presence of an effective reducing agent. These factors decrease the tendency for carbon dioxide to evolve from soil organic matter, in part from decarboxylation reactions (5) as well as by an oxidation induced by reactions between the added acid and manganese dioxide native to the soil (1, 2). Absorption of the gas in a measured excess of standard barium hydroxide solution is practically concurrent with its evolution in the closed system, minimizing opportunity for losses. The absorption is quantitative, and with normal soils there is no error from absorption of any other acid. A simple titration of the barium hydroxide not precipitated as barium carbonate is, therefore, an accurate index of carbonates in the sample. Conducted as described, the procedure is of particular value as a qualitative test for carbonates. In many instances, the determination need not be finished, as the absence of the characteristic precipitate of barium carbonate shows that no carbonate is present. With operation *in vacuo*, any gas bubbles produced by the decomposition of carbonate minerals are greatly magnified, and useful information as to the nature of the carbonate in a sample may sometimes be gained from observations on the rate and circumstances of such evolution. Cessation of visible action is a good index of complete decomposition; the progress of absorption can likewise be noted, and in these features the method presents unique advantages.

Although for soils containing high magnesium limestone, dolomite, or magnesite, this method is not so rapid as a steam distillation procedure recently described (4), its indications are still considered a standard of accuracy. The slower decomposition of the carbonate minerals noted is attributable to the lower temperature at which the reaction proceeds. For most soils the rate of decomposition of carbonates is as rapid as could reasonably be desired and the other operations are not unduly time-consuming. For these reasons, and for its value as a delicate qualitative test, the method is suitable for use in the routine examination of soils as well as when the carbonate content must be determined with the highest degree of accuracy.

The most important improvement over the original specifications for the apparatus is the substitution of a condenser tube with eight oval bulbs for the straight tube first described. The increase in efficiency of condensation thus obtained is less important than the elimination of difficulties commonly encountered when liquids are boiled under a high vacuum, and which occasionally caused the loss of a determination with the straight condenser. Boiling *in*

vacuo, the soil and acid mixture is likely to be projected into the condenser, and a part of it may even be shot into the absorption flask. But with a bulbed condenser, this latter accident is very unlikely to happen. The liquid may be thrown upward, but as it passes through successive bulbs its progress is checked, and hence, with a proper rate of boiling, these slugs of liquid will be stopped at less than half the height of the condenser.

APPARATUS

The apparatus required is shown in figure 1. The inner tube of the condenser *C* is made of 13-mm. o. d. glass tubing, 1.2-mm. wall. Eight oval bulbs, each of approximately 10 ml. capacity, are blown in that part of the tube which will be within the outer jacket of glass tubing 28 mm. o. d. and 42 cm. long. These parts are connected by rubber stoppers, also bored for glass tubes 5 mm. o. d., for circulation of water in the condenser jacket. Above and at the minimum distance necessary to avoid burning the upper stopper, is sealed to the bulbed inner tube a semicircular side arm, bent to a radius of approximately 5.5 cm. as shown. The tube is cut off about 10 cm. above this seal and finished with a slight flare, to take a No. 00 stopper. The other end of the bulbed inner tube is cut off at a point which will be about 12 cm. below the lower rubber stopper at the condenser jacket, and is finished with only a slight taper so that backflow of liquid thrown up into the condenser will not be impeded. Number 8 rubber stoppers, bored for a tight fit with the 13-mm. condenser tube and side arm and 5-mm. o. d. tubes for addition of reagents, are attached at the lower ends of the condenser tube and side arm above. Lengths of high-quality rubber tubing, $\frac{1}{4}$ -inch heavy wall steam-cured, are attached to the 5-mm. o. d. glass tubes and provided with Day pinchcocks *D* and *E*. The lower No. 8 stopper fits the sample flask *A*, a 250-ml. Pyrex extraction flask, sufficiently heavy to be evacuated with safety even though flat-bottomed; the stopper on the side arm holds the absorption flask *B*, a standard 1-liter, round-bottom, short ring-neck Pyrex "balloon flask."

At the top of the condenser hangs the small vacuum gauge shown in detail at *G*. This is easily made by sealing concentrically two thin-walled glass tubes of suitable size, the larger easily fitting inside the condenser, the smaller about 3 cm. long, finishing the seal with a neat ring for suspension, and blowing a hole in the outer tube near the seal before annealing. The outer tube is finally drawn to a taper and sealed, making the finished gauge about 5 cm. long. To ensure satisfactory performance by such a small gauge, interior clearances for mercury flow must be at least 1.5 mm. To fill, sufficient clean mercury is added through the hole in the outer tube. The gauge is suspended in the condenser tube by a substantial nichrome wire threaded through the lower part of a No. 00 rubber stopper also carrying a glass tube bent as shown, with rubber tube and Day pinchcock *X*. On exhausting the apparatus to the practical capacity of the pump, air is drawn out of the inner tube of the gauge, so that mercury enters when the pressure is restored; thereafter, sufficient evacuation of the apparatus is indicated by fall of the mercury to about the same level. The gauge is not calibrated, as it serves only as a rough indicator of internal pressure or to show the presence of considerable unabsorbed carbon dioxide, air from a leak, or inefficient condensation.

The assembly of evolution and absorption flasks connected by the verticle condenser is supported by a heavy retort stand or similar means, and a single large rubber-faced clamp grips the tape-wound condenser jacket near the bottom. The assembly is sufficiently flexible to allow agitation with a rotary motion, thus swirling the liquids in the flasks and speeding evolution and absorption of carbon dioxide.

Other parts of the apparatus are:

(*H*) An automatic zero-point pipette, connected by a siphon tube to the barium hydroxide solution bottle, all mounted on shelves at a convenient height above the apparatus. This pipette must always be filled and emptied in the same way, for a constant delivery of about 50 ml. of the solution.

(I) A bead-filled gas washing tower containing a strong solution of potassium hydroxide, for scrubbing the air admitted to the apparatus when breaking the vacuum.

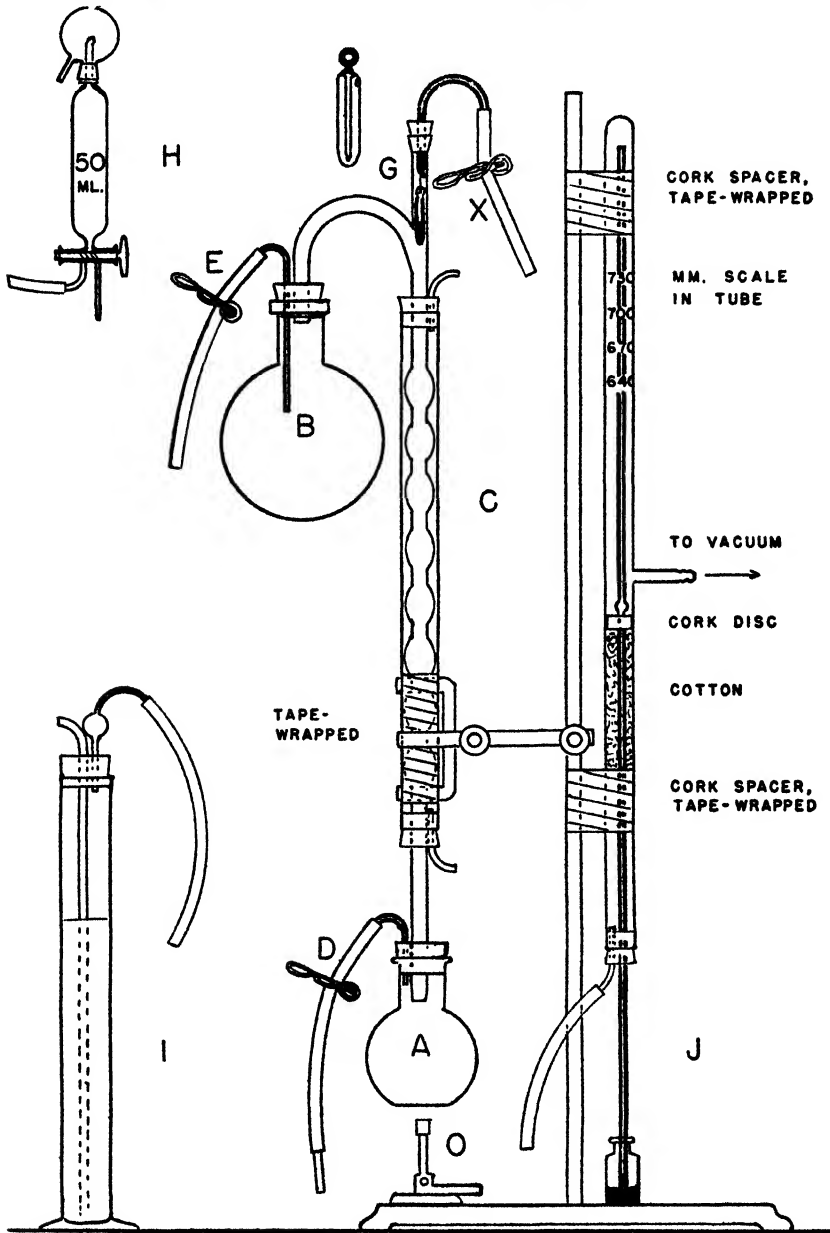


FIG. 1. APPARATUS FOR THE DETERMINATION OF CARBONATES IN SOIL
(See text for detailed description)

(J) A barometric gauge to indicate the performance of the vacuum pump, also serving as a trap to stop dust or liquids from being drawn into the working parts of a mechanical pump. The construction will be evident from the figure.

(O) The small flame required to boil the contents of flask A is supplied by a microburner and protected from drafts by a shield made by cutting the top and one side from a tin can.

No vacuum pump is shown in the figure. A good water jet aspirator may serve, but a motor-driven, oil-sealed "Cenco Hyvac" rotary air pump is used in this laboratory. It should be noted that with continued use much water vapor is drawn through the pump, and a part of this condenses in the oil reservoir, either displacing the oil or being emulsified with it. The state of the oil must be watched, with renewal when necessary or the water drawn off before it causes the oil to overflow. A medium heavy motor oil may be used; with moisture present, there is no point in using the special low-vapor-pressure vacuum pump oil. The vapor pressure of water at 30°C. is about 32 mm. mercury, and therefore a gauge reading within 32 mm. of the barometer reading is good performance. Rusting of the steel working parts of the pump may be reduced by adding to the oil a little powdered potassium dichromate, which will dissolve in any water present and act as a corrosion inhibitor.

REAGENTS

Barium hydroxide solution. Prepare a 6.5 per cent solution of the crystals in hot water and let stand until cold and clear. Carefully siphon this nearly saturated solution—about 0.4 *N*—into a bottle containing sufficient boiled and cooled water to make the finished mixture slightly less than 0.2 *N*. Insert the siphon tube connected to the delivery pipette and add to the bottle pure paraffin oil to make a 2–3-mm. layer over the surface. As an additional precaution against absorption of carbon dioxide from air entering the bottle, connect a soda lime or similar trap to the stopper. The overflow bulb of the delivery pipette should have similar protection, to ensure maintenance of slightly appearance and constancy of delivery.

Decinormal hydrochloric acid. Made with CO₂-free water and accurately standardized. For this titration, it is conveniently delivered from an M. C. A. chamber burette, having a 50-ml. bulb below the zero graduation and graduated 50–100 ml. in 0.1-ml. intervals.

1:1 hydrochloric acid. The concentrated reagent diluted with an equal volume of water. This approximates the constant boiling point acid, sp. gr. 1.1, and can be handled without much annoyance from fumes.

Ferrous chloride solution. Put about $\frac{1}{2}$ pound steel turnings or nails in a $\frac{1}{2}$ -gallon bottle and cover with 1 liter 1:1 hydrochloric acid. Add a few drops of antifoam and set aside until action ceases. Pour off the solution, boil to expel hydrogen sulfide, etc., and filter into a 1-liter bottle. Cover the solution with oil to retard oxidation. The clear green solution is about 3 *N*. If it turns yellow or if a heavy red precipitate appears, the original strength can be restored by adding sufficient 1:1 hydrochloric acid to clear, and reducing again with iron as described.

Shaw and MacIntire (4) recommend stannous chloride (5 per cent SnCl₂·2H₂O in the 1:10 hydrochloric acid used for decomposing carbonates) as the reducing agent to prevent oxidation of organic matter in the soil carbonate determination. They say that the extent of the error from action on organic matter can be judged from the depth of yellow color in the acid solution from which the soil has settled following their steam distillation procedure for carbonate determination. This is not possible when ferrous chloride is the deoxidant, as the ferric chloride then present has a similar strong color. With stannous chloride, the presence of sufficient for maximum effect should be indicated by a minimum yellow color in the solution settled clear after decomposing carbonates. A further advantage possibly important under some circumstances is that with stannous chloride there should be no evolution of hydrogen sulfide with carbon dioxide if the sample happens to contain sulfide.

An aqueous solution of stannous chloride saturated at room temperature is approximately 3 *N* in reducing power and may be substituted for the ferrous chloride solution originally specified.

Indicator solution. A 0.5 per cent solution of either thymolphthalein or phenolphthalein in neutral 95 per cent ethanol—the same for both the blank titration and that with the sample—may be used. The former indicator has the theoretical advantage that its point of decolorization is near pH 9, whereas the corresponding point for phenolphthalein is about one pH unit lower. In a titration of barium hydroxide in the presence of suspended barium carbonate, hydrolysis of the latter causes a high pH value to persist beyond the point of neutralization of excess hydroxide, hence the indicator turning at the higher pH should be preferable. To reach the point of decolorization of phenolphthalein, an appreciable concentration of bicarbonate must be built up. Titration to decolorization of phenolphthalein causes low indications, from the persistence of the color after the addition of an amount of acid which should be sufficient for its discharge. Titration to a definite color end point, pH 8.35, by matching against a buffer solution at that pH and with the same phenolphthalein concentration and about the same amount of barium carbonate in suspension, has been shown to give accurate indications (4). The simpler titration to decolorization of thymolphthalein is correct in theory but has the practical disadvantage of a gradually fading blue tint as the titration progresses. It is difficult to distinguish between a very faint blue and a pure white. In a blank titration with little suspended barium carbonate, there is further complication from a faint Tyndall blue caused by precipitation of the indicator. In practice, good results are obtained by titrating to disappearance of blue when there is much barium carbonate in suspension, and to the point where the very faint blue is not further diminished by an additional drop of acid in the case of a blank.

Antifoam. A mixture of equal volumes of capryl alcohol (Eastman Kodak Co., No. P66) and light mineral oil; a drop or two added from a small oiler is effective in causing persistent foam to subside.

Distilled water. As the water furnished by most laboratory stills may be expected to contain more carbon dioxide than corresponds to equilibrium with normal air, 0.05 mgm. CO₂ in 100 ml., removal of CO₂ by boiling is advisable.

PREPARATION OF SAMPLE

A soil containing carbonates may possibly have only a few fragments of calcareous material in a considerable volume; grinding is necessary, therefore, to ensure analytical samples of uniform composition. The time required to decompose the carbonate in a sample containing coarse particles resistant to attack by cold acid, *e.g.*, of dolomite, may be excessive. Hence, it is desirable to have the carbonates ground as fine as is practical. Fortunately, the carbonate minerals likely to occur in soils are soft and easily reduced, compared to quartz grains and the like. From 15 to 30 minutes' rotation in a stoneware jar mill with flint pebbles in proper proportion to the amount of soil, at a rate ensuring efficient grinding, has usually been sufficient for satisfactory uniformity and ease of decomposition, in the writer's experience. But it has often been necessary further to grind in a mortar the portion remaining on a sieve with 0.5-mm. round holes, when coarse particles of resistant limestone were found to survive grinding in the jar. In such cases, the ground residue is added to the fine material and again ground in the jar mill for further reduction and thorough mixing. Coarse sandy soils containing carbonates are sometimes very troublesome, from difficulty in reducing hard grains and segregation of the finely ground calcareous material. Such samples should be reduced in amount by the use of a riffle and finally ground all to pass 100-mesh.

Since the soil water is likely to contain bicarbonate or free carbon dioxide, highly accurate indications for carbonate content can be expected only from

dried samples of soil. It has been said that air-dry soil may retain carbon dioxide in the adsorbed state (6). Shaw and MacIntire (4) recognize the possibility, as they direct that the weighed portion of air-dry ground sample in the flask to be connected to the carbonate apparatus shall be kept in a desiccator over flake sodium hydroxide for an hour before proceeding with the determination; they offer no comment on the necessity for this precaution. Alexander and Byers (1) report experiments wherein 0.003–0.008 per cent carbon dioxide was obtained, by aspiration for 1 hour, from samples of various soils suspended in water. This was assumed to represent adsorbed carbon dioxide. It may be pointed out, however, that some of this may have been derived from another source; evolution of carbon dioxide from calcareous material in contact with moist unsaturated soil is known to proceed rapidly. The soils under discussion were acid, pH 5.0–5.7, but appeared to contain small amounts of carbonate. In the procedure for carbonate determination described in the following section, the assembled apparatus containing the air-dry sample is well evacuated and swept with water vapor as a preliminary operation, and reliance is placed upon this treatment to remove any carbon dioxide adsorbed by the sample as well as that in the air initially in the apparatus. The very low apparent carbonate content indicated for soils probably containing no mineral carbonate is accepted as evidence that this is sufficient.

PROCEDURE

Transfer a suitable weight of the sample, 20 gm. or more if the soil is very low in carbonate but not more than the equivalent of 0.25 gm. CaCO_3 , to flask *A*. If difficulty from excessive foaming is expected, add a drop of antifoam. Attach the glass-tipped rubber tube *D* to the rubber tube of trap *J*. Moisten the rubber stopper and attach flask *A* securely. Also attach the empty flask *B* in the same way and apply vacuum by removing pinchcock *D*, so that air pressure will seat both stoppers firmly and prevent the flasks falling. As soon as gauge *G* indicates vacuum, attach rubber tube *E* to the tip of filled pipette *H*, open pinchcock *E* momentarily, then stopcock *H* fully. Open *E* cautiously to empty *H* at a proper rate for reproducible delivery, and draw all the barium hydroxide solution from *H*, but close *E* before air passes. Close *H* and open *E* for a moment, so that expansion of air in the tip of *H* will drive the last of the solution past *E*. Pinch the rubber tube *E* near its end with the fingers and detach it from *H*. Dip *E* into a 50-ml. beaker full of distilled water and open *E* cautiously, so that nearly all the water but no air is drawn into *B*. By this time, *G* should indicate exhaustion to the capacity of the vacuum pump. The solution just added to *B* at room temperature may be boiling under the reduced pressure and the vapors condensing in the upper part of *C*, through which a plentiful supply of cold water should be circulating. Replace pinchcock *D* and detach the tube from *J*. Hold a 50-ml. beaker filled with distilled water under *X* and allow about half the water to be drawn into the apparatus. If the sample is not completely wetted at once, shake with a slight rotary motion to swirl the contents of *A*. Wash down any dust that may have arisen into *C* by adding nearly all the remainder of the water through *X*. Into a second 50-ml. beaker, used for this purpose alone, pipette 5 to 10 ml. of the ferrous or stannous chloride solution, add 5 to 20 ml. of 1:1 hydrochloric acid and fill the beaker with water without mixing the contents.¹ Dip tube *D* to the bottom and allow the heavier layer of chloride

¹ The amounts of chloride solution and of hydrochloric acid to be used will depend upon the size and nature of the sample and the carbonate mineral present. Large samples high in manganese dioxide require more chloride, and for samples containing dolomite the acid

solution to enter flask *A* with sample, following with the acid slowly lest the action become too violent. If the evolution of carbon dioxide is very vigorous, wait for this to abate and cautiously swirl the mixture in flask *A* before adding the rest of the acid and water. When it seems safe to do so, swirl to mix thoroughly. If much carbon dioxide has been evolved, this will already have entered *B*, and a crust of barium carbonate will be seen on the solution therein. Swirl the contents of *B* with caution; if absorption of carbon dioxide is too rapid, the mixture in *A* may become unmanageable. Set the microburner *O*, with soft flame about 1 cm. high, under *A*. Boiling will begin almost at once, and foam may arise into *C*, especially if no antifoam has been added. If it seems necessary, add a drop of this through *X*, followed by a spurt of water to wash it down. Regulate the boiling at a safe rate, with vapors rising not higher than about the middle of the condenser. As long as much carbon dioxide is being evolved from the acid mixture, boiling will be quiet; when evolution ceases, violent bumping will begin. At this point, remove the flame and after the mixture becomes quiet examine it closely. If there is no evidence of action upon isolated particles of carbonate minerals, let the water out of the condenser jacket and resume the boiling until vapor passes into *B*, meanwhile swirling the absorbent solution therein. When no further formation of barium carbonate is noted after standing for a minute or two, the absorption of carbon dioxide may be considered practically complete. Connect *D* to the potassium hydroxide tower *I* and break the vacuum, cautiously at first then removing pinchcock *D* and admitting air as rapidly as it will pass through the semicapillary glass tube at the top of *I*. Meanwhile support *B* with the hand and give its contents a swirling motion. Detach tube *D* from *I*, then flask *B* from the rubber stopper. Wash down the outside of the glass tubes in *B* with a spurt of water, lower *B* and insert a No. 8 stopper with one hole closed by a glass plug. Shake vigorously for a minute, to ensure absorption of every trace of carbon dioxide. Remove the glass plug, add about 0.5 ml. indicator solution, then insert the delivery tip of the burette containing decinormal hydrochloric acid and start the titration. Add the acid at the usual rate with constant motion, until a decolorized area appears in the swirling liquid. At this point, cease the addition of acid, replace the glass plug, and shake well. Resume the titration with increasing caution as the end point is approached. Just prior to complete decolorization, stop and shake the flask as before. The distinctly blue thymolphthalein color remaining should be discharged by a further addition of two or three drops of decinormal acid. The difference between this titration figure and that obtained in an identical procedure without a sample indicates the carbonate content of the sample. One milliliter of 0.1 *N* acid corresponds to 2.2 mgm. CO_2 , equivalent to 5.0 mgm. CaCO_3 or 0.6 mgm. *C*.

REFERENCES

- (1) ALEXANDER, L. T., AND BYERS, H. G. 1932 A critical laboratory review of methods for determining organic matter and carbonates in soil. U. S. Dept. Agr. Tech. Bul. 317.
- (2) SCHOLLENBERGER, C. J. 1930 Increased accuracy in the determination of carbonates in soil. *Science* 72 (1853): 13-14.
- (3) SCHOLLENBERGER, C. J. 1930 Determination of carbonates in soil. *Soil Sci.* 30: 307-324.
- (4) SHAW, W. M., AND MACINTIRE, W. H. 1943 Steam distillation—a new procedure for the determination of carbonate CO_2 . *Jour. Assoc. Off. Agr. Chem.* 26: 357-396.
- (5) SHORRY, E. C., AND MARTIN, J. B. 1930 The presence of uronic acids in soils. *Jour. Amer. Chem. Soc.* 52: 4907-4915.
- (6) WHITNEY, R. S., AND GARDNER, R. 1943 The effect of carbon dioxide on soil reaction. *Soil Sci.* 55: 127-141.

concentration should be greater. The object in any case is to use no more acid than necessary to ensure decomposition of carbonates in a reasonable time. If insufficient acid was added at the start and the decomposition of carbonate is slow, indicating that dolomite may be present, more acid can be added through *D*.

DETERMINATION OF SOLUBLE SALTS IN SOILS¹

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The procedure to be used in determining soluble salts in soils depends on the accuracy and detail required. Total dissolved solids may be determined by evaporation of a soil solution or extract. Estimation of total soluble salts is often made from the electrical conductivity of a soil solution or extract of the moist soil itself. Determination of the composition of the soluble salts is made by chemical analysis. The ions usually included in such analyses are Ca, Mg, Na, CO₃, HCO₃, SO₄, and Cl. Among those less commonly determined are K, NH₄, and NO₃.

The units employed in reporting quantities of soluble salts are equivalents per million³ (e.p.m.), parts per million (p.p.m.), and per cent. All are on a weight basis when referred to the soil. Because the salts are soluble and presumed to be completely dissolved in the soil solution or in the aqueous extract, the analyses are sometimes expressed as concentrations in these solutions. In such cases the units are usually equivalents per million, milliequivalents per liter, and parts per million. Equivalents per million is the most satisfactory unit because it is on a chemical combining basis, analyses can be quickly checked for accuracy by comparing sums of cations and anions, conversion of salt contents from a solution to a soil basis is facilitated, and plant response is more closely correlated with salt content on an equivalent basis than on a weight basis. Equivalents per million, on a soil or solution basis, and milliequivalents per liter, on a solution basis, are converted to parts per million by multiplying by the appropriate equivalent weight. For a 1:1 soil extract, equivalents per million in the extract and in the soil are numerically equal. Some laboratories may prefer to report salt contents in parts per million on the dry soil basis.

MOISTURE PERCENTAGE

The total quantity and the proportion of various ions present in the soil solution often vary with the moisture percentage. Thus the total quantity of Ca and SO₄ ions dissolved from a gypsiferous soil increases with successive

¹ Contribution from the U. S. Regional Salinity Laboratory and the Division of Irrigation Agriculture, Riverside, California, Bureau of Plant Industry, Soils and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture, in cooperation with the eleven Western States and the Territory of Hawaii.

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³ An equivalent per million is a unit chemical equivalent weight of salt per million unit weights of soil or of solution. When referred to a solution, e.p.m. and m.e./l. are numerically identical where the specific gravity of the solution is 1.0. In almost all work with soil solutions the percentage difference between the true specific gravity and 1.0 is less than the analytical error. The unit was defined in A.S.T.M. standards—1940, part III, p. 541.

additions of water. Similar increases for certain ions are found on increasing the proportion of water to soil when the soils are calcareous or contain appreciable amounts of replaceable sodium. To illustrate these phenomena, data from unpublished work by Reitemeier are presented.

In figure 1-A the total quantity of each ion dissolved, in terms of equivalents per million of soil, found at various moisture percentages, is plotted as ordinate

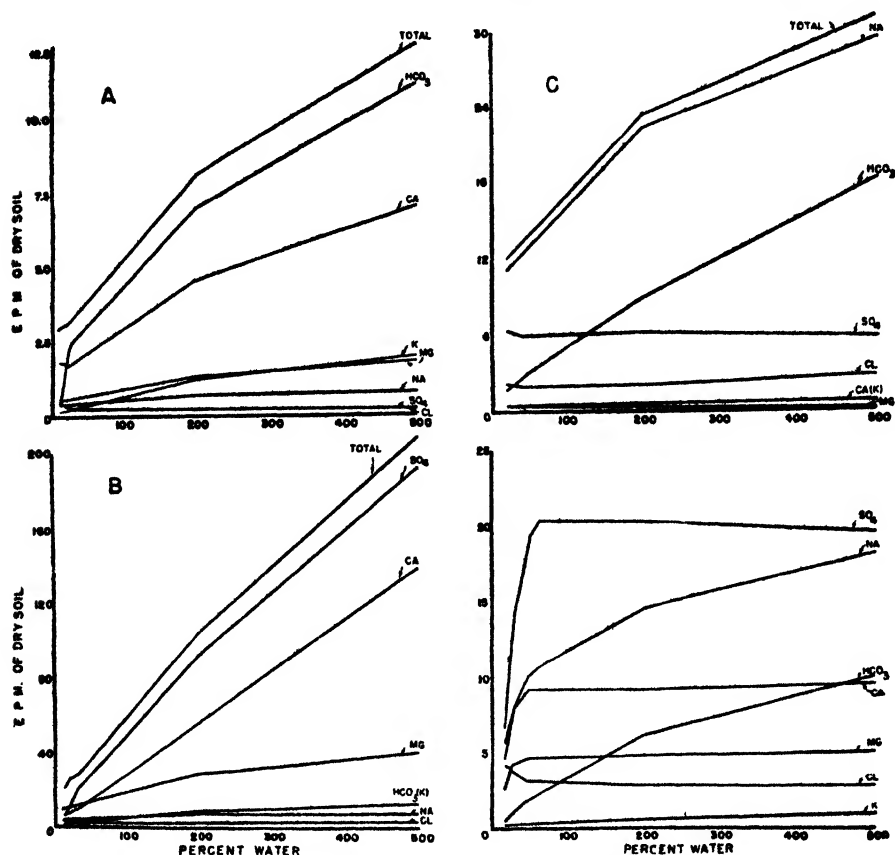


FIG. 1. VARIATION OF DISSOLVED SALTS WITH MOISTURE PERCENTAGE

A. Hesperia sandy loam; B. Reagan clay loam; C. Indio very fine sandy loam; D. Imperial clay. Results expressed in gram-equivalents per million grams of oven-dry soil.

against the moisture percentage as abscissa for Hesperia sandy loam. This soil is slightly calcareous but does not contain gypsum or an appreciable amount of replaceable sodium. As the water is increased from 8 per cent (wilting point 4.7 per cent) to 500 per cent the total amounts of Ca and HCO₃ ions found in solution also greatly increase. In this case, analysis of a 1:5 soil extract (500 per cent water) would, on extrapolation, give a distorted picture of the amount of calcium and bicarbonate present in the soil solution at normal field moisture content.

Reagan clay loam (fig. 1-B) contains gypsum and calcium carbonate and very little replaceable sodium. Extracts of this soil contain far more total Ca^{++} and SO_4^{--} than at 14 per cent, the lowest moisture content shown (wilting point 11.4 per cent).

Indio very fine sandy loam (fig. 1-C) contains calcium carbonate and a considerable quantity of replaceable sodium. On dilution from 21 per cent (wilting point, 6.1 per cent) to 500 per cent the total HCO_3 content increases because increased amounts of calcium carbonate are dissolved. Most of this calcium replaces exchangeable sodium, and as a result there is only a slight increase in total Ca in solution with increased dilution, but a large increase in sodium. Eaton and Sokoloff (7) have drawn attention to this phenomenon. An increase in exchangeable calcium and an equivalent increase in soluble sodium may occur as a result of dilution alone, as shown by Magistad, Fireman, and Mabry (9).

Results for Imperial clay are shown in figure 1-D. This soil contains gypsum, calcium carbonate, and replaceable sodium. The water content of this soil ranged from 17 (wilting point 15.1 per cent) to 500 per cent. The amount of gypsum present is small and all is dissolved when the moisture content is about 60 per cent. With increasing water content above this percentage Imperial clay behaves similarly to the Indio soil.

The above examples show that in order to obtain an accurate picture of the concentrations of certain ions in the soil solution at moisture contents between the wilting percentage and field capacity, the solution for analysis should be obtained without further dilution. This is especially true for soils containing calcium carbonate, gypsum, or appreciable amounts of replaceable sodium.

METHODS OF OBTAINING THE SOIL SOLUTION

It is apparent from figure 1 and the foregoing discussion that the composition of the soil solution varies considerably with soil moisture content. If water is added to the soil, the nature of the resulting solution changes considerably from the solution originally present in the soil. The greater the amount of water added, the wider are the differences. Because of this, it is important to keep the water content as near as possible to that existing in the soil in the range of interest.

Displaced soil solutions

Soil solutions existent in soils at field moisture contents can usually be obtained by displacement with water or alcohol. The use of alcohol was discussed by Parker (11), and an aqueous displacement method was described by Burd and Martin (4). Soils which are readily puddled require excessive periods for extraction of sufficient solution, and the majority of soils cannot be used at moisture contents near the wilting range.

The essential points of the method follow. A brass tube of about 3 inches diameter and 17 inches length is fitted with a filter paper, wire screen, and a threaded cap having an opening for the escape of the displaced solution. The

inside of the tube is greased with a light cup grease to prevent channeling along the sides. The well-mixed soil is added to the tube in portions of about 100 gm. and tamped after each addition to secure a sufficiently dense soil column. A free space of about 8 inches is left above the soil. Several hundred milliliters of water or alcohol is added above the soil. (Sometimes when water is used, acetylacetone or a soluble thiocyanate is added to it as a tracer to test the displaced solution for contamination with the displacing liquid; to make this test, a solution of ferric iron is added to a drop of the displaced solution.) With some soils, displacement proceeds under the force of gravity alone. The successive portions of displaced solution are collected in fractions of about 25 ml. and their conductivity is determined. Fractions of about the same conductivity can be composited for analysis. A sharp change in conductivity usually indicates contamination with the displacing liquid.

Many soils require pressure to yield adequate rates of flow. Provided the apparatus is built to withstand the pressure, air is introduced above the displacing liquid up to a maximum of 100 pounds of pressure per square inch. For this purpose, both ends of the displacement tubes must be fitted with pressure-tight gaskets and threaded caps. The top cap is provided with a $\frac{1}{2}$ -inch connection for entry of air.

Pressure-membrane solutions

A recent method for obtaining soil solution, which involves a combination of high gas pressure and a cellophane membrane, has been described by Richards (14). Detailed directions for its operation and discussion of its reliability under different conditions have been published by Reitemeier and Richards (13). The method has proved very useful for saline soils. With regard to extraction of fine-textured soils and soils of low moisture content, the method appears superior to the customary displacement procedure. Volumes of solution obtained usually are small, and the semimicroanalytical methods of Reitemeier (12) have generally been used for their analysis.

Water extracts

Many laboratories are not equipped to obtain soil solutions by means of displacement or the pressure-membrane method and may wish to choose methods which are more rapid but less precise. This would be especially true where many soils are to be analyzed. In such cases water extracts at the saturation percentage or at a 1:1 ratio (100 per cent water) are suggested.

Extracts at the saturation percentage. An extract from most soils at the saturation percentage can be obtained by filtration on a Büchner funnel at percentages somewhat below 100. The National Resources Planning Board in its Pecos River Joint Investigation (10) included a salinity survey under the direction of C. S. Scofield, who used extracts obtained at the saturation percentage. This is a fairly reproducible water content, varying from less than 20 per cent

for sands up to 60 or 80 per cent for most clays. The saturation percentage is determined by Scofield (15, p. 9) as follows:

One hundred grams of the dry soil are weighed into a soil can having a tight cover. Distilled water is added and the soil is stirred with a spatula until a condition of saturation is reached. In its saturated condition the soil mass should be plastic enough to flow slightly when the container is tipped. The surface should glisten as it reflects light, and the air should all be displaced. The can with its saturated soil is again weighed, and the increase in weight from the dry condition is recorded as "water required to saturate" in terms of percentage of the dry weight of the soil.

For macroanalytical methods 150 ml. of extract is recommended. To obtain this, 1 to 2 kgm. of dry soil is needed. Filtration can be performed on a large-sized Büchner funnel or a small filter press. If semimicroanalytical methods are used, 200 gm. of soil will suffice.

To the soil in a mixing bowl or other suitable container gradually add distilled water with stirring until the saturation percentage is reached. Remove a small subsample for moisture determination. After standing over night to obtain equilibrium, filter by means of a small filter press or Büchner funnel prepared as when filtering soil extracts. Turbid filtered extracts will sometimes clear on standing, or may be filtered through a Pasteur-Chamberland filter.

The extracts are analyzed by methods listed in the following pages.

The volume of the solution obtained depends on the moisture content of the soil and the time allotted for its extraction. Analysis of the solution can be made by the methods outlined in the following pages, if sufficient sample is available; otherwise, semimicro-analytical methods such as those described by Reitemeier (12) are recommended.

1:1 Soil extract. The use of a 1:1 soil extract is less precise than the extract at the saturation percentage, but may be chosen where many determinations are to be made and high accuracy is not required. Since equal weights of solution and soil are used, calculations are reduced to a minimum.

Add 1,500 gm. of dry soil or its equivalent to 1,500 ml. of water (including the water held by the soil) in a bottle of suitable size.⁴ Stopper, and shake at intervals for several hours by hand or shake for $\frac{1}{2}$ hour on a mechanical shaker, and filter on a Büchner funnel. A medium grade of filter paper may be used. First moisten the paper with distilled water to prevent soil material creeping under it. It is advisable to use a water aspirator pump to provide suction, as a dry vacuum system may remove some water by evaporation. During filtration, cover the funnel with a watch glass. Discard the first portion of filtrate.

ANALYSIS OF SOIL SOLUTION OR SOIL EXTRACT

Total dissolved solids

A determination of total dissolved solids is usually made to obtain a measure of the total salinity, and serves as a check against the results of chemical analysis and of electrical conductivity. Total dissolved solids are determined by evaporating a portion of the extract to dryness and weighing. The residue may

⁴ In a few cases of exceptionally heavy soils a 1:1 extract yields little solution on filtering. In such cases a 1:1.5 or 1:2 extract may be necessary.

include water of crystallization, soluble organic matter, silica, and any other dissolved material.

Procedure (1, p. 525). Evaporate 100–250 ml. of extract to dryness in a weighed platinum or porcelain dish. Dry to constant weight at 110° C. Cool and weigh. If a 100-ml. sample of a 1:1 extract is used, grams of residue $\times 10,000$ equals parts per million on the solution and on the dry-soil basis. The residue can be utilized for analyses of cations, if the volume of extract or solution available is limited.

Specific electrical conductance

The electrical conductivity of solutions is dependent on the number and kinds of ions and accordingly serves as a measure of total salinity.

The specific electrical conductance (K) is reported in reciprocal ohms per centimeter, and for soils work is customarily multiplied by 10^5 to avoid awkward decimals. Thus, for example, the conductivity of a soil extract can be indicated as $K \times 10^5$ @25° C. = 134.

An approximation of the total salt concentration in equivalents per million may be obtained by dividing the conductivity ($K \times 10^5$ @25° C.) by 10. If the conductivity is multiplied by 7, the resulting value approximates total dissolved salts expressed in parts per million. Thus, in water with a conductivity of 100, the sum of equivalents per million of CO_3 , HCO_3 , SO_4 , Cl , and NO_3 will be about 10, and the total dissolved salts will be about 700 p.p.m.

The equipment required for making conductivity measurements, and its operation, are described by the following authors: Daniels, Mathews, and Williams (5), Davies (6), Scofield (15), and Wilcox.⁵

For purposes of comparison, all conductivity values are referred to 25° C. The conductivity bridge actually measures electrical resistance, and this decreases with increasing temperature. At ordinary temperatures, this decrease amounts to approximately 2 per cent per degree Centigrade. Correction for temperature can be avoided by use of a constant temperature bath maintained at 25° C, or by using a reference solution at the same temperature as the unknowns.

Conductivity of saturated soil paste. Recent unpublished work has shown this determination to be lacking in reliability and it is recommended that the conductivity of a soil extract be substituted.

ANALYSIS OF EXTRACT

Suggested volume

For an analysis that includes the determination of calcium, magnesium, sodium, potassium, carbonate, bicarbonate, sulfate, and chloride, the suggested volume of extract is:

Low conductivity ($K \times 10^5$ = less than 100): 600 ml.

Moderate conductivity ($K \times 10^5$ = 100 to 500): 300 ml.

High conductivity ($K \times 10^5$ = 500 and over): 150 ml.

⁵ Wilcox, L. V. 1942 *Methods of Analysis used in the Rubidoux Laboratory*, ed. 4. U. S. Dept. Agr., Bureau of Plant Industry, Division of Irrigation Agriculture. [Mimeographed.]

Colored solutions

Colored extracts are sometimes encountered. In such extracts it is difficult to obtain the correct end point in the carbonate, bicarbonate, and chloride titrations. If the amount of organic matter present is great and seriously interferes with the titration, it is recommended that carbonate and bicarbonate be titrated electrometrically. Dilution of such colored extracts sometimes permits better end points, but errors are correspondingly increased. Under such conditions chlorides can be determined gravimetrically. Though it might appear that soluble organic matter would interfere seriously with the determination of other ions, experience has shown that the error involved is slight even for deeply colored extracts.

Silica, iron, and aluminum

Extracts from neutral or moderately alkaline soils usually contain too little silica, iron, and aluminum to interfere with the determination of the ions listed above. For extracts from acid soils, strongly alkaline soils, turbid extracts, or those of very low salt content, the removal of silica, iron, and aluminum according to the directions given elsewhere in this issue⁶ is suggested.

*Calcium (3 modified)**Reagents*

- (a) Hydrochloric acid (1 + 1).
- (b) Oxalic acid solution, *N*.
- (c) Ammonium hydroxide (1 + 1).
- (d) Sulfuric acid, concentrated.
- (e) Standard potassium permanganate, 0.05 *N*.

Procedure. Acidify 100 ml. of the extract with HCl (a). (Volumes suggested for each ion are based on an extract of moderate conductivity.) Add 1 ml. oxalic acid solution (b) and heat to boiling. Neutralize with ammonium hydroxide (c). Add an excess (10 ml. is usually sufficient) of oxalic acid solution gradually with constant stirring. Add ammonium hydroxide to the hot solution until just alkaline to methyl orange. Allow to cool and stand for several hours. During the cooling, further additions of ammonium hydroxide may be necessary to keep the solution faintly alkaline to methyl orange. Filter through quantitative paper and wash thoroughly with water until the washings are free from chloride. Save the filtrate and washings, designated as solution A, for magnesium. Puncture the tip of the filter paper and wash the precipitate into a clean beaker. (The beaker in which the calcium was precipitated can be used if free of chloride.) Dilute 5 ml. concentrated sulfuric acid (d) to 50 ml. with water, and pour this hot solution through the filter paper. Wash with several portions of water or until the volume is approximately 100 ml. Heat nearly to boiling and titrate with the standard potassium permanganate solution (e) to a faint pink color. When the end point is reached, drop the filter paper into the solution, and stir thoroughly. Complete the titration quickly to the first definite pink end point. Subtract a blank, usually about 0.15 ml. Report as Ca in equivalents per million. If 100 ml. of extract is used, the net volume of 0.05 *N* KMnO₄ in milliliters multiplied by 0.5 will equal Ca in equivalents per million.

*Magnesium (1, p. 537, modified)**Reagents*

- (a) Hydrochloric acid (1 + 1).
- (b) Diammonium hydrogen phosphate solution, 10 per cent. A fresh lot of this reagent should be prepared for each set of samples.

⁶ See Robinson, W. O. The fusion analysis of soils.

- (c) Ammonium hydroxide (1 + 1).
- (d) Ammonium hydroxide, concentrated.
- (e) Dilute ammonium hydroxide (1 + 49).

Procedure. Neutralize solution A to methyl orange with hydrochloric acid (a) and add 2 ml. in excess. Evaporate to a volume of about 50 ml. and allow to cool. Add 10 ml. of the diammonium hydrogen phosphate reagent (b). The solution should be slightly acid at this point. Add ammonium hydroxide (1 + 1), drop by drop with stirring, until a precipitate begins to form or until the solution is strongly alkaline. After a few minutes, add 15 ml. concentrated ammonium hydroxide. On the following day, filter on ashless paper and wash with dilute ammonium hydroxide (e). Transfer the paper with the precipitate to a weighed silica or porcelain crucible, dry, ignite, and weigh as $Mg_2P_2O_7$. Report as Mg in equivalents per million. If 100 ml. of extract is used, the weight in grams of $Mg_2P_2O_7$ multiplied by 179.7 = Mg in equivalents per million.

Sodium (2 modified)

Reagents

(a) Uranyl zinc acetate reagent: uranyl acetate ($2 H_2O$), 300 gm.; zinc acetate ($2 H_2O$), 900 gm.; acetic acid, 30 per cent, 270 ml.; water 2,430 ml. Transfer the salts to a large flask and add the acetic acid and water. Shake or stir until the salts are dissolved. This may take several days. Filter just before use.

(b) Ethyl alcohol saturated with sodium-uranyl-zinc-acetate precipitate. Filter just before use. This solution decomposes gradually on standing.

(c) Ether, anhydrous, c.p.

Procedure. Transfer to a Pyrex beaker, an aliquot of the extract sufficient to give 50-200 mgm. of the triple salt (usually 10-20 ml.). Neutralize with acetic acid and evaporate to about 1 ml. (Should the residue become dry, silica may be dehydrated and interfere with filtration; for that reason, evaporation to dryness should be avoided.) Cool. Add 20 ml. of the filtered reagent (a). Stir the solution and allow to stand 1 hour, or longer with repeated stirring if the quantity of precipitate is very small. Filter through a porcelain filtering crucible. Transfer the precipitate to the filter by means of a small wash bottle filled with filtered reagent. Wash the beaker 5 times with 2-ml. portions of the filtered reagent and add the washings to the crucible. It is important to have the crucible and the precipitate free of the reagent before washing with alcohol. As soon as the reagent has drained away completely, wash the crucible 4 times with 2-ml. portions of the saturated alcohol (b). Remove the alcohol by suction and wash twice with ether (c). Continue the suction until the precipitate is dry. Allow the crucible to stand in a desiccator 1 hour and weigh. Return the crucible to the suction apparatus and wash with small portions of water until all the soluble material is dissolved and has passed through the crucible. Wash with alcohol and ether, dry and weigh, as before. The difference between the two weighings represents the weight of the sodium precipitate. A blank should be determined by the same procedure. Report as Na in equivalents per million; if a 10-ml. aliquot of the extract is used, the net weight of the triple salt in grams multiplied by 65.02 = Na in equivalents per million. The triple salt is represented by the formula: $(UO_2)_2ZnNa(CH_3COO)_6 \cdot 6H_2O$. The procedure, as described, reduces errors due to small amounts of phosphate.

Potassium (16)

Reagents

(a) Nitric acid, N.

(b) Trisodium cobaltinitrite solution. Prepare an aqueous solution containing 1 gm. of the salt of reagent quality in each 5 ml., allowing 5 ml. for each determination. Filter before use. The solution is stable for some time, but it is preferable to make up a fresh lot before each set of determinations.

(c) Nitric acid, 0.01 N.

(d) Ethyl alcohol, 95 per cent.

Procedure. Transfer 10-50 ml. of the extract to a Pyrex beaker. Add a few drops of dilute sodium hydroxide and evaporate to dryness to eliminate ammonium ion, which inter-

feres with the determination of potassium. Add 10 ml. water and neutralize with nitric acid (a). After the salts are in solution, add 1 ml. of *N* nitric acid and 5 ml. of the sodium cobaltinitrite solution (b). Mix and allow to stand for 2 hours, or longer if the quantity of precipitate is very small, at not over 20° C. Filter through a glass or porcelain crucible of fine porosity, the tare weight of which is known, using 0.01 *N* nitric acid in a wash bottle to make the transfer. Wash 10 times with 2-ml. portions of the dilute nitric acid and 5 times with 2-ml. portions of alcohol. The temperature of the wash solutions should be the same as the samples. Continue the suction until the alcohol is removed and the precipitate is dry. Wipe the outside of the crucible with a cloth, dry for 1 hour at 110° C., cool in a desiccator, and weigh. Report as K in equivalents per million. If a 20-ml. aliquot of the extract is taken, the weight of the precipitate in grams multiplied by 220.2 = K in equivalents per million. The precipitate can be represented by the formula: $K_2NaCo(NO_2)_6 \cdot H_2O$.

Carbonate and bicarbonate (1, p. 535, modified)

This determination is sometimes referred to as total alkalinity because phosphates, borates, and silicates are included in the titration. Usually the amounts present are too small to cause appreciable errors.

Procedure. To 50 ml. of the extract, add a few drops of phenolphthalein, and if a pink color is produced, titrate with 0.05 *N* sulfuric acid, adding a drop every 2 or 3 seconds until the pink color disappears. Multiply the burette reading in milliliters by 2 to obtain carbonate in equivalents per million. To the colorless solution from this titration, or to the original solution if no color is produced with phenolphthalein, add 1 or 2 drops of methyl orange, and without refilling the burette continue the titration to the first change in methyl orange color, and note the total reading. Designate the solution as B and reserve for determination of chloride. If carbonate is absent, the total burette reading in milliliters is numerically equal to bicarbonate in equivalents per million. If carbonate is present, multiply the reading with phenolphthalein by 2 and subtract this figure from the total reading of the burette. The difference in milliliters is numerically equal to equivalents per million of bicarbonate. Blank determinations should be run with the reagents and corrections made if necessary. Report as CO_3 and HCO_3 in equivalents per million. In samples containing small amounts of carbonate in the presence of much larger amounts of bicarbonate, the calculation of the normal carbonate concentration in the above manner involves considerable percentage error. It is suggested that under such conditions the concentration of carbonate be calculated from Hirsch's carbonate-equilibria slide rule (8).

Chloride (1, p. 528, modified)

Reagents

(a) Potassium chromate indicator. Dissolve 5 gm. K_2CrO_4 in water and add a saturated solution of silver nitrate until a slight permanent red precipitate is produced. Filter and dilute to 100 ml.

(b) Silver nitrate solution, standard 0.05 *N*.

Procedure. To solution B from the bicarbonate determination, add 1 ml. potassium chromate indicator (a) and titrate with standard silver nitrate solution (b) to the first tinge of reddish brown. Correct for the quantity of silver nitrate solution necessary to give, in 50 ml. of chloride-free water with 1 ml. of chromate indicator, the shade obtained at the end of the titration of the sample. Report as Cl in equivalents per million. If a 50-ml. aliquot of the extract is taken, the net volume in milliliters is numerically equal to equivalents per million of Cl.

Sulfate (1, p. 537 modified),

Reagents

(a) Concentrated hydrochloric acid.

(b) Barium chloride solution, 10 per cent.

Procedure. Neutralize an aliquot (50–100 ml.) of extract with hydrochloric acid to methyl orange and add 1 ml. in excess. Make the volume to 100 ml., if necessary. Heat

to boiling and add an excess of BaCl_2 solution (b) drop by drop with constant stirring. Cover with a watch glass and allow to stand on the water bath for several hours, during which the volume should be reduced to about 50 ml. After cooling, filter the precipitate of BaSO_4 through fine-textured ashless filter paper and wash with water until free of chloride. Transfer the filter paper to a tared porcelain crucible, and place in a cold, well-ventilated muffle furnace, which is slowly brought to red heat. After complete ignition of the paper, remove the crucible, cool, and weigh. A blank determination should be run. Report as SO_4 in equivalents per million. The net weight of BaSO_4 precipitate in grams multiplied by 85.7 equals equivalents per million of SO_4 if a 100-ml. aliquot is used.

Accuracy of analysis

An estimate of the precision or reproducibility that may be expected for each determination from the above methods, under ordinary conditions, is shown in table 1. This table is based on studies made independently by two

TABLE 1

Maximum deviations from the mean that may be expected in the course of triplicate analyses of the same sample—the deviations may be either negative or positive

	IONS OR SUBSTANCE DETERMINED							
	$K \times 10^5$	TDS*	Ca	Mg	Na	HCO_3	SO_4	Cl
		p.p.m.	s.p.m.	s.p.m.	s.p.m.	s.p.m.	s.p.m.	s.p.m.
Concentration	50	350	2.0	2.0	2.0	2.0	2.0	2.0
Deviation.....	1	10	0.05	0.1	0.02	0.1	0.1	0.1
Concentration	500	3,500	20.0	20.0	20.0	5.0	20.0	20.0
Deviation.....	5	50	0.1	0.2	0.05	0.15	0.2	0.2

* Total dissolved solids.

workers and represents the experience of several years and many thousands of water analyses. The data indicate the deviation which may be expected on any individual determination.

A check on the accuracy of the analysis as a whole is to compare the sum of cations with the sum of anions. Failure to agree may be due to omission of some ion, relatively important, such as K, NH_4 , NO_3 . The total soluble salts in parts per million calculated from the analysis should agree roughly with total dissolved solids, with due regard for organic matter, water of crystallization, silica, and conversion of bicarbonate to carbonate in the T.D.S. determination. The American Public Health Association in its *Methods for Examination of Water and Sewage* (p. 54, 1936) point out:

The sum of the milliequivalents of basic radicals must obviously equal the sum of the milliequivalents of acid radicals. In routine practice a variation from 15 per cent in waters of less than 50 p.p.m. residue down to a 2 per cent variation in waters over 1,000 p.p.m. residue, may be expected.

Since the methods described above for soil extracts are similar to those of the American Public Health Association for water, it can be expected that the results will be of the same order of accuracy.

REFERENCES

- (1) Association of Official Agricultural Chemists 1940 Official and Tentative Methods of Analysis, ed. 5. Washington, D. C.
- (2) BARBER, H. H., AND KOLTHOFF, I. M. 1928 A specific reagent for the rapid gravimetric determination of sodium. *Jour. Amer. Chem. Soc.* 50: 1625-1631.
- (3) BLASDALE, W. C. 1909 The quantitative separation of calcium from magnesium. *Jour. Amer. Chem. Soc.* 31: 917-922.
- (4) BURD, J. S., AND MARTIN, J. C. 1923 Water displacement of soils and the soil solution. *Jour. Agr. Sci.* 13: 265-295.
- (5) DANIELS, F., MATHEWS, J. H., AND WILLIAMS, J. W. 1934 Experimental Physical Chemistry. McGraw-Hill Book Co., New York.
- (6) DAVIES, C. W. 1930 The Conductivity of Solutions. John Wiley & Sons, New York.
- (7) EATON, F. M., AND SOKOLOFF, V. P. 1935 Absorbed sodium in soils as affected by the soil-water ratio. *Soil Sci.* 40: 237-247.
- (8) HIRSCH, A. A. 1942 A slide rule for carbonate equilibria and alkalinity in water supplies. *Indus. and Engin. Chem., Analyt. Ed.* 14: 943-946.
- (9) MAGISTAD, O. C., FIREMAN, M., AND MABRY, B. 1944 Comparison of base-exchange equations founded on the law of mass action. *Soil Sci.* 57: 371-379.
- (10) National Resources Planning Board 1942 The Pecos River Joint Investigations: Reports of the Participating Agencies. Washington, D. C.
- (11) PARKER, F. W. 1921 Methods of studying the composition and concentration of the soil solution. *Soil Sci.* 12: 209-232.
- (12) REITEMEIER, R. F. 1943 Semimicroanalysis of saline soil solutions. *Indus. and Engin. Chem., Analyt. Ed.* 15: 393-402.
- (13) REITEMEIER, R. F., AND RICHARDS, L. A. 1944 Reliability of the pressure-membrane method for extraction of soil solution. *Soil Sci.* 57: 119-135.
- (14) RICHARDS, L. A. 1941 A pressure-membrane extraction apparatus for soil solution. *Soil Sci.* 51: 377-386.
- (15) SCOFIELD, C. S. 1932 Measuring the salinity of irrigation waters and of soil solutions with the Wheatstone bridge. U. S. Dept. Agr. Cir. 232.
- (16) WILCOX, L. V. 1937 Determination of potassium by means of an aqueous solution of trisodium cobaltinitrite in the presence of nitric acid. *Indus. and Engin. Chem., Analyt. Ed.* 9: 136-138.

DETERMINATION OF TOTAL COPPER, ZINC, COBALT, AND LEAD IN SOILS AND SOIL SOLUTIONS

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Copper, zinc, and cobalt occur in small quantities in all soils. Copper and zinc are essential to plant growth. Cobalt, though not proved essential to plant growth, apparently is essential to normal animal development. Lead in small quantities is of general occurrence in plants and soils. Because of the important role these minor constituents play in both plant and animal life, it is often desired to know the contents of these elements in the soil and in soil solutions.

Each of these four elements belongs to a group of metals known to react with dithizone (diphenylthiocarbazone), under certain conditions, to form colored compounds when dissolved in carbon tetrachloride or chloroform. They are subject, therefore, to the dithizone system of isolation and analysis. Many analysts have investigated the determination of some of these constituents with dithizone. The following procedures are based largely on the work of Wichmann (9), Cowling (5), Clifford (4), Greenleaf (8), Bamback (1), Bendix (3), Ellis (7), and Cronheim (6).

OUTLINE OF METHOD

The analytical procedure proposed for the determination of copper, zinc, cobalt, and lead is depicted in figure 1. Though this diagram shows all the important steps to be taken in determining the quantities of these constituents in a soil, it tells nothing about technique and equipment, purification of chemicals, glassware, and sources of contamination that inadvertently enter, all of which require serious consideration.

EQUIPMENT AND REAGENTS

Technique and equipment

Technique in this work is acquired with experience, though to some extent inherent in the analyst. The amount of equipment required depends somewhat on the number of analyses to be made. It is essential to have three times the number of separatory funnels as the number of samples to be analyzed simultaneously. The separatory funnel most suited to this work is the Squibb type, Pyrex, 125-ml. At least two 4-liter Pyrex separatory funnels also are required for the preparation of dithizone reagent, the purification of other chemicals with dithizone, and other uses. An efficient mechanical shaker for the 125-ml. funnels is indispensable if many determinations are to be made. The shaker should be designed to make about 300 strokes per minute through a space of 1½ inches. All liquid reagents should be kept in Pyrex glass. Rubber stoppers

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should not be used in any place. The importance of redistilled water, hydrochloric acid and nitric acid, and ammonia from an all-Pyrex still is emphasized by almost all analysts in this field. All water used in the making of these reagents should be redistilled.

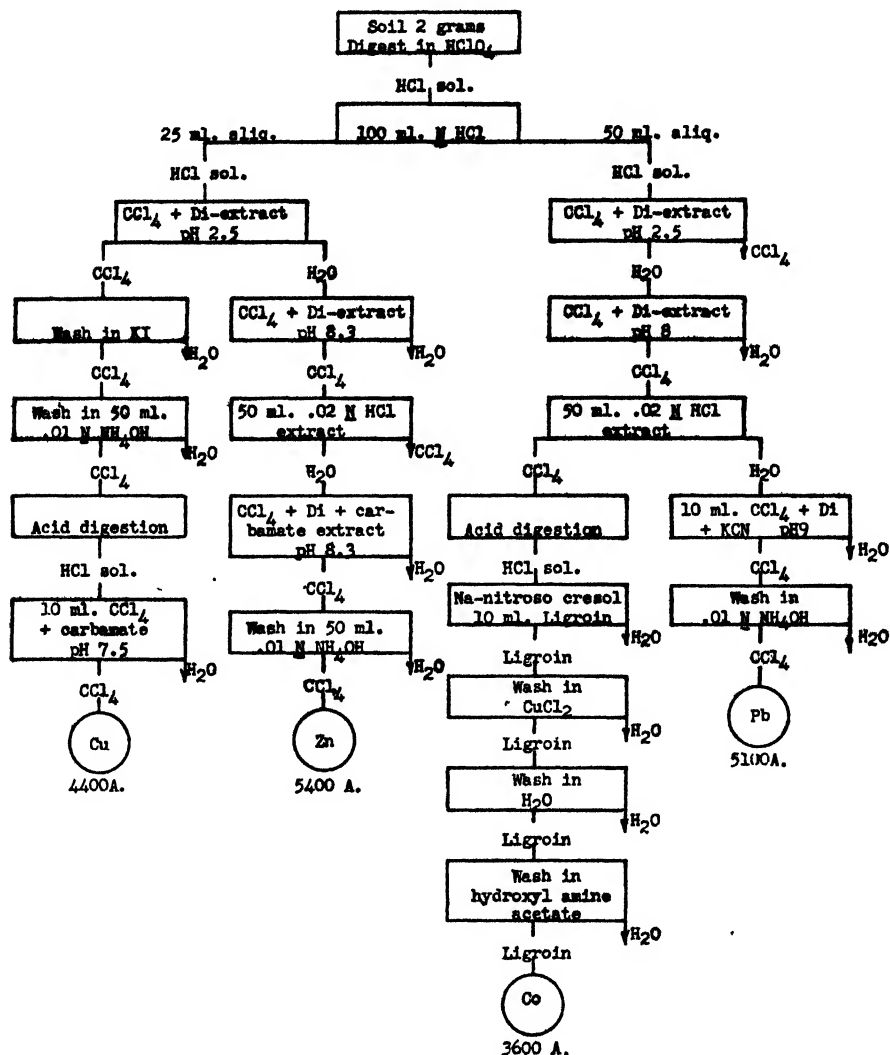


FIG. 1. DIAGRAM FOR THE DETERMINATION OF COPPER, ZINC, COBALT, AND LEAD

Reagents

Hydrochloric acid may be purified and reduced to known concentration by distilling a mixture of 1-to-1 hydrochloric acid and distilled water from an all-Pyrex still and collecting for use as standard the portion that distills at constant temperature. Normal acid is easily prepared from the constant boiling distillate.

Ammonium hydroxide. Distill concentrated ammonium hydroxide into water in a Pyrex container immersed in an ice-bath. Pure ammonium hydroxide of known concentration may also be prepared by passing anhydrous ammonia from a cylinder of liquid ammonia through a dry liter filtering flask into a second container of cooled water. The concentration may be had by weighing the water before and after the gas is added.

Ammonium citrate buffer (25 per cent solution). Dissolve 225 gm. of ammonium citrate $[(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7]$ in 1 liter of water using a large separatory funnel as a container. Add concentrated ammonia (40 to 45 ml.) until the solution has a pH of 8.5. Purify by repeated extractions with dithizone reagent and remove excess dithizone with repeated extractions with pure CCl_4 .

Sodium borate buffer (for Co). Dissolve 20 gm. of boric acid in 1 liter of water and add 22 ml. of $N \text{ H}_2\text{SO}_4$. The pH should be approximately 7.5.

Potassium iodide solution (for Cu), 2 per cent. Dissolve 10 gm. of c.p. potassium iodide in 490 ml. of water. Acidify by adding 5 ml. of $N \text{ HCl}$. Add 5 ml. of 0.1 N sodium sulfite to reduce the free iodine. Shake in separatory funnel with successive 10-ml. portions of dithizone reagent until no discoloration of dithizone occurs. Discard the dithizone extract and remove excess dithizone by repeated extractions with CCl_4 . If upon standing free iodine should occur in this solution, it should be reduced with Na_2SO_3 or removed with CCl_4 .

Hydroxylamine sodium acetate solution (for Co). Dissolve 10 gm. of $\text{NH}_2\text{OH} \cdot \text{HCl}$ and 9.5 gm. of sodium acetate in 500 ml. of water. If the pH is not between 5 and 5.2, it should be adjusted with NaOH or acetic acid.

Carbon tetrachloride. C.p. carbon tetrachloride may be used without purification. Technical and used CCl_4 may be purified by first washing it in dilute HCl and then in 0.02 $N \text{ NH}_4\text{OH}$, drying it with anhydrous calcium chloride, and distilling.

Petroleum ether and ligroin (for Co). These two solvents may be purified in the same manner. Place about 2.5 liters in a large separatory funnel and shake with successive portions of H_2SO_4 until the H_2SO_4 is colorless. Wash three times with distilled water and distill, collecting for use the portion of petroleum ether that distills between 45° and 65° C., and the portion of ligroin that distills between 70° and 90° C.

Dithizone reagent. Dissolve 0.25 gm. of diphenylthiocarbazon in 1 liter of carbon tetrachloride, using a 4-liter separatory funnel as a container. After it has stood for at least 15 minutes with frequent agitation, add 2 liters of 0.02 N ammonia (40 ml. of $N \text{ NH}_3$ to 2 liters), then extract the dithizone into the aqueous phase by vigorous shaking. Discard the CCl_4 phase, and extract the ammoniacal solution of dithizone with 50-ml. portions of CCl_4 until the CCl_4 is a pure green color. Discard the CCl_4 phase after each extraction. Add 500 ml. of CCl_4 and 50 ml. of $N \text{ HCl}$ and shake to transfer the dithizone into the CCl_4 phase. Dilute the CCl_4 -dithizone solution to 2 liters with CCl_4 and store in a Pyrex bottle that has been painted black, or thoroughly covered with black paper. It is well to add to this reagent 25 ml. of water partly saturated with sulfur dioxide.

Carbamate reagent (for Cu and Zn). Dissolve 0.2 gm. of sodium diethyl dithiocarbamate in 100 ml. of water. Filter into a separatory funnel and shake with 5-ml. portions of pure CCl_4 to remove copper. Prepare a fresh solution for each use.

Sodium nitrosocresol reagent (for Co). The sodium nitrosocresol is prepared from the copper salt of *o*-nitrosocresol. The *o*-nitrosocresol is easily prepared by the Baudisch reaction (2). Using a 4-liter separatory funnel, dissolve 6 gm. of $\text{NH}_2\text{OH} \cdot \text{HCl}$, 15 gm. of CuCl_2 in 900 ml. of distilled water. Add 5 ml. of meta-cresol and thoroughly mix. These proportions are important in that they give the best pH for the reaction. Then add 15 ml. of 30 per cent H_2O_2 with stirring. After shaking thoroughly and allowing to stand for 2 hours at room temperature, add 25 ml. of concentrated HCl and shake. Add 100 ml. of petroleum ether and shake for 1 minute. Draw off the aqueous phase into another clean funnel and repeat the extraction with successive portions of petroleum ether until all of the reagent is extracted. Combine the yellow portions of petroleum ether, now containing the *o*-nitrosocresol, in the first funnel and wash three times by shaking with successive portions of distilled water. Discard the water, and extract the reagent from the petroleum ether into a

water solution of copper acetate. This is done by shaking the petroleum ether with 100-ml. portions of a 1 per cent solution of copper acetate. Repeat this extraction until the petroleum ether becomes colorless. Four times should be sufficient. The combined aqueous extracts of the copper complex should be of deep red color. Filter this solution and store it in a refrigerator as stock solution. It will keep under these conditions without decomposition.

Sodium nitrosocresol reagent is prepared from the copper nitrosocresol stock solution. For a set of 12 samples, transfer 75 ml. of the stock nitrosocresol to a separatory funnel and add 10 ml. of HCl. Add 500 ml. of petroleum ether. Shake thoroughly to transfer the *o*-nitrosocresol solution to the petroleum phase. Discard the water phase and wash the petroleum ether phase twice with 100-ml. portions of 0.01 *N* HCl and twice with 100-ml. portions of water. Discard the water. Add 50 ml. of the sodium borate buffer and 2 ml. of *N* NaOH and shake. Repeat this extraction if necessary to remove the *o*-nitrosocresol from the petroleum ether. Combine the aqueous extracts of the sodium nitrosocresol reagent for the cobalt.

Standard solutions of copper, zinc, cobalt, and lead

A stock solution (100 γ per milliliter) of each of these metals is prepared in the following manner:

Copper. Accurately weigh 0.1 gm. of electrolytic sheet copper or any pure metallic copper, and dissolve it in 10 ml. of dilute nitric acid. Evaporate the solution almost to dryness and add 2-3 drops of glacial acetic acid. Transfer the solution quantitatively to a 1-liter volumetric flask, fill to mark with water, and thoroughly mix.

Zinc. Place exactly 0.1 gm. of pure zinc in a 1-liter volumetric flask, dissolve in a mixture of 50 ml. water and 1 ml. concentrated sulfuric acid. Dilute to the mark and thoroughly mix.

Lead. Place 0.1598 gm. of dried (110° C.) recrystallized c.p. $\text{Pb}(\text{NO}_3)_2$ in a 1-liter volumetric flask, dissolve in 1 per cent nitric acid and fill to the mark with the nitric acid, and thoroughly mix.

Cobalt. Dehydrate about 5 gm. of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in an electric oven at 250° to 300° C. to constant weight (6 to 8 hours is sufficient). Place exactly 0.263 gm. of the CoSO_4 in a 1-liter volumetric flask and dissolve in a mixture of 50 ml. water and 1 ml. H_2SO_4 . Fill to the mark with redistilled water and mix thoroughly.

From the standard stock solutions of copper, zinc, cobalt, and lead, a less concentrated working standard is prepared. Usually the most convenient working standard contains 1 γ of the metal per 1 ml. This solution is prepared by pipetting out exactly 10 ml. of the stock solution into a 1-liter volumetric flask and making up to the mark with water.

ANALYTICAL PROCEDURE

Preparation of sample

Pass a well-mixed air-dried sample through a 2-mm. iron sieve. Then quarter it down to 5 to 10 gm. and grind it in an agate mortar to pass through a 100-mesh bolting cloth sieve. No metal alloy apparatus containing copper, zinc, cobalt, or lead should be used in collecting or preparing the soil sample.

Decomposition of soil

Digest 2 gm. of soil in HClO_4 (60 per cent) for 1 hour at boiling temperature, then raise the temperature and adjust the cover glass so that the acid fumes can escape. Evaporate the solution almost, but not quite, to dryness. The high temperature and reduced volume are essential to dehydrate silica without its retention of any metals sought. Cool the flask, add 50 ml. of *N* HCl, and boil under refluxing conditions for 20 to 30 minutes. Cool the solution somewhat, and decant it through a filter into a 100-ml. volumetric flask. Wash the residue repeatedly with small portions of hot *N* HCl which is decanted through filter

into flask until flask is filled to mark. The manner and time of digesting the soil are important to thorough decomposition and dehydration. This has been accomplished conveniently in a 100-ml. wide-mouth Erlenmeyer flask covered with a reflux cover glass as shown in figure 2.³ This cover causes a continuous return of the condensed acid vapor to the center of the digestion flask, which prevents spattering and lessens the tendency to bump. It has been found very useful in the wet-ashing of plant material.

The insoluble residues of soils from HClO_4 digestion investigated by the author have been found to contain only traces of these four constituents, copper, zinc, cobalt, and lead. It is possible that there are soils high in certain unweathered minerals which are not sufficiently decomposed by the HClO_4 digestion. In such cases, the insoluble residue is transferred to a platinum dish, decomposed with repeated treatments with hydrofluoric acid, evaporated to dryness, taken up with N HCl , and added to the first.

Determination of copper and zinc

Separation of copper and zinc (3, 5, 8). Pipette a suitable aliquot of the sample solution into a 125-ml. separatory funnel. An aliquot equivalent to 0.5 gm. of soil is found satisfactory in most cases. Add 5 ml. of the 10 per cent ammonium citrate buffer. Titrate the

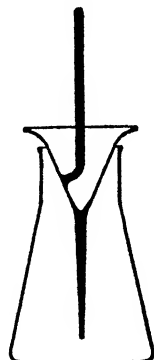


FIG. 2. REFLUX COVER GLASS

acidity of the solution with ammonia to pH 2.5, using thymol blue, acid range, as an indicator. Immediately after adding the indicator, add the ammonia until the red color of the indicator begins to turn yellow. Add exactly 5 ml. of dithizone solution and shake for 5 minutes. Transfer the CCl_4 phase to a clean separatory funnel, and if the first extraction shows a considerable excess of free dithizone, repeat the extraction with a less concentrated dithizone solution. Combine the two dithizone extractions for the copper determination and retain the aqueous phase for the zinc determination.

Add to the copper dithizone solution 10 ml. of the acidic potassium iodide solution and shake for 2 minutes. This is to remove bismuth and other metals that form complex ions with iodine. Transfer the copper dithizone phase to a clean separatory funnel, and free the copper dithizonate from the excess dithizone by shaking for 1 minute with 50 ml. of 0.01 N NH_4OH .

Copper. The copper may be determined at this point as the dithizonate or carbamate. To estimate it as the dithizonate, the percentage transmission is made of the ammonia-washed copper dithizonate using a light filter of 5,200 Å. From the reading, determine the amount of copper from a prepared standard curve relating light transmission to concentration.

³ This cover glass was suggested and made by L. Testa, the glassblower at the Bureau of Plant Industry, and its use in this procedure was developed by R. B. Deemer.

Since carbamate is a more specific reagent for copper than the dithizone, it is preferred by many analysts. Transfer the ammonia-washed copper dithizonate quantitatively to a Berzelius tall-form 100-ml. beaker with spout. Add 0.5 ml. of concentrated HNO_3 , cover with a watch glass, and evaporate on the water bath. Add 0.5 ml. of HClO_4 , and evaporate on the hot plate until almost all (but not necessarily all) the HClO_4 is driven off. Cool and add 10 ml. of water and boil to remove all traces of HNO_3 . Transfer solution from beaker to separatory funnel by rinsing with hot N HCl . Add 2 or 3 drops of phenolphthalein or cresol red solution and titrate with ammonia to pH 8.5. Add 5 ml. of the carbamate solution and exactly 10 ml. of CCl_4 , shake for 3 minutes, and allow the layers to separate. Draw off the CCl_4 phase through a loose pledget of cotton placed in the dried stem of the separatory funnel. Determine the transmission in a suitable photometer using a filter of 4,400 Å. From a calibration curve estimate the amount of copper present.

Zinc. The zinc is retained quantitatively in the aqueous phase saved from the copper extraction. To this solution add 5 ml. more of the ammonium citrate buffer, and raise the pH to 8.3 by titrating with ammonia, using phenolphthalein as an indicator. More ammonium citrate solution may be added if necessary to prevent precipitation of iron and aluminum. Extract the zinc with two or more 10-ml. portions of dithizone solution. When the zinc is completely removed, the aqueous phase will be orange, and the last dithizone extraction should show no color characteristic of zinc dithizonate. Remove the last floating drop and adhering droplets of the dithizone by shaking with pure CCl_4 . Combine all zinc dithizonate extracts in a clean separatory funnel. Discard the aqueous phase.

To extract the zinc into 0.02 N HCl , add 50 ml. of 0.02 N HCl and shake for 2 minutes, then allow the phases to separate. Draw off the CCl_4 phase as completely as possible without letting any of the water phase enter the stopcock bore. Rinse out all adhering dithizone with pure CCl_4 . Discard the CCl_4 phase.

To extract zinc in the presence of carbamate, add 5 ml. of ammonium citrate buffer to the 50 ml. of 0.02 N HCl extract, and titrate with ammonia to pH 8.3, using phenolphthalein as indicator. Add exactly 10 ml. of dithizone reagent and 10 ml. of the carbamate reagent, shake for 2 minutes, and allow the phases to separate. Transfer the zinc dithizonate phase to a clean funnel. Remove excess dithizone by shaking with 25 ml. of 0.01 N NH_4OH . Allow the phases to separate completely. Pipette exactly 5 ml. of the zinc dithizonate from near the bottom of the phase into a colorimeter cell and dilute with CCl_4 to 25 ml. The 5 ml. of zinc dithizonate is easily removed from the funnel without removing the aqueous phase by inserting the dry pipette through the aqueous phase while a current of air is forced downward through the pipette. Determine the light transmission of the diluted solution with a suitable photoelectric colorimeter, using a filter of 5,400 Å. and setting 100 per cent transmission for pure CCl_4 , not the 100 per cent for the blank. A blank determination should be run with each series of zinc determinations. From the standard curve, estimate the amount of zinc present in both the blank and the unknown. Subtract the blank and multiply the remainder by the reciprocal of the fractional gram of soil represented by the 5 ml. of zinc dithizonate diluted. In the typical case as here outlined, the reciprocal is 4.

Determination of cobalt and lead

Usually a soil contains less cobalt and lead than copper or zinc; therefore, a larger aliquot is needed for the determination of cobalt and lead. For soils containing very small quantities of lead, several grams will have to be used as a sample to enable an accurate determination. In such cases, proportionally more HClO_4 is used in the digestion, and more ammonium citrate buffer is added to the more concentrated soil solution when working at a pH of 6.5 or above. The following procedure is for a 50-ml. aliquot, which is equivalent to 1 gm. of soil. Transfer the 50-ml. aliquot to the separatory funnel. Add 5 ml. of ammonium citrate and titrate with ammonia to pH 2.5, using thymol blue, acid range, as indicator. Add ammonia until the red color of the indicator just turns yellow. Add 5 ml. of the dithizone reagent and shake for 5 minutes. Allow the aqueous and the dithizone

phases to separate completely. Drain out and discard the dithizone phase as completely as possible without allowing the water to enter the stopcock bore. Repeat this extraction. This is to remove the copper, bismuth, and other metals that form dithizonates at pH 2.5. The cobalt, lead and, zinc are retained quantitatively in the aqueous phase. To the aqueous phase add 5 ml. more of the ammonium citrate buffer and titrate with ammonia to pH 8.5, using thymol blue, basic range, as indicator. Add 10 ml. of dithizone reagent and shake from 1 to 2 minutes. Allow the phases to separate. Draw off the dithizone phase into a second funnel and repeat the extraction until the last extract is a distinct clear green. Combine the dithizone extracts in the second funnel and discard the aqueous phase.

Separation of cobalt and lead (1, 4, 6, 7). To the combined dithizone extract add 25 ml. of 0.02 *N* HCl and shake for 2 minutes. Retain the acid extract in the funnel, but run out the dithizone phase in a second funnel and repeat the acid extraction. Draw off the dithizone phase as completely as possible into a third funnel and save for the cobalt determination. Transfer the acid extract from the second funnel into that retained in the first. Wash the combined acid extracts with 1-2 ml. of pure CCl₄ and run CCl₄ into the dithizone saved for cobalt determination. The lead and certain other metals are now in the acid extract. The cobalt is in the dithizone extract.

Cobalt. Transfer the cobalt dithizone extract to a Berzelius tall-form 100-ml. beaker with spout. Add 0.5 ml. concentrated HNO₃, cover with a watch glass, and evaporate on a water bath. Add 5 ml. of HClO₄, evaporate on a hot plate until all HClO₄ is driven off. Cool and add 10 ml. of 0.02 *N* HCl, warm to effect solution, and transfer solution from beaker to funnel quantitatively by washing the beaker with 5-10 ml. of water. Neutralize with 10 ml. of sodium borate buffer.³ Add 0.5 ml. of the Na-nitrosocresol reagent and shake.⁴ If there is not a dominant orange color over that of the violet color formed, add a few drops more of the reagent. Add exactly 10 ml. of ligroin and shake for 5 minutes. Allow the two phases to separate thoroughly and discard the aqueous phase without loss of ligroin. Add 10 ml. of 4 per cent CuCl₂ solution, shake for 1 minute, and discard the aqueous phase. Add 25 ml. of redistilled water, shake, and discard the water. Add 5 ml. of hydroxylamine sodium acetate solution, shake for 1 minute, and discard the aqueous phase. The hydroxylamine reduces any ferric complex that might be present to ferrous, which is water-soluble and is eliminated from the ligroin-soluble Co-nitrosocresol. The aqueous phase is separated from the ligroin as completely as possible. A small portion of ligroin is allowed to pass through the funnel stem, the remainder is filtered, through a pledget of cotton placed in the stem of the funnel, into the colorimetric cell. Determine the transmission in the spectrophotometer at 3,600 Å. with blank at 100 per cent transmission. The quantity of cobalt is estimated from a prepared curve relating light transmission and cobalt concentration.

Since the maximum light absorption of the cobalt nitrosocresol ligroin solution is about 3,600 Å., the measuring of its color is not easy. The author obtained satisfactory readings with a Coleman Model 10 spectrophotometer, set at 3,600 Å. transmission. The color of the cobalt nitrosocresol dissolved in ligroin obeys Beer's law over a wide range of concentrations. The solution may be diluted or concentrated. Either the blank or pure ligroin may be used as 100 per cent transmission or reference liquid.

Lead (1, 4). The lead is determined in the acid aqueous extract saved from the cobalt

³ The resultant solution should have a pH of 7.5. The appearance of the sodium nitrosocresol reagent when added to the solution serves very well as an indicator. In an acid solution, it is a pale yellow. In a neutral or alkaline solution, it is a deeper yellow or orange. If the solution is found to be too acid, adjust the pH by adding NaOH, as the presence of the ammonium ion inhibits the formation of the Co-*o*-nitrosocresol.

⁴ This method for the determination of cobalt as the Co-*o*-nitrosocresol compound is based on the work of Cronheim (6) and of Ellis (7). The *o*-nitrosocresol is a rather specific reagent for cobalt, since only the cobalt, ferric, and palladium compounds of it are soluble in petroleum ether.

determination. First add 5 ml. of ammonium citrate and then 10 ml. of 10 per cent KCN solution, and titrate with ammonia to a pH of 9.3, using thymol blue as indicator. Titrate to maximum blue color of indicator. Add exactly 10 ml. of dithizone reagent and shake for 3 minutes. Transfer the CCl_4 phase to a clean funnel and wash with 50 ml. of 0.01 N NH_4OH to remove excess dithizone. Run a small quantity of the lead dithizonate solution through the stem of the funnel and the remainder through a pledget of cotton placed in the stem. Measure the light transmission in a photoelectric colorimeter using 5,100 Å. filter, and estimate the quantity of lead from a prepared curve relating light transmission and lead concentration.

A standard curve is prepared from data obtained by placing 0, 5, 10 . . . ml. of the working standard solution in separatory funnels and proceeding in exactly the same manner as used in determining the unknown. Measure the percentage transmission, and plot the logs of the percentages of the ordinate against concentration expressed in micrograms on the abscissa.

REFERENCES

- (1) BAMBACK, K., AND BURKEY, R. E. 1942 Microdetermination of lead by dithizone. *Indus. and Engin. Chem., Analyt. Ed.* 14: 904-908.
- (2) BAUDISH, O. 1941 Preparation of *o*-nitrosophenol from benzene or other aromatic hydrocarbons at room temperature. *Jour. Amer. Chem. Soc.* 63: 622.
- (3) BENDIX, G. H., AND GRABENSTITTER, D. 1943 A dithizone method for the rapid determination of copper. *Indus. and Engin. Chem., Analyt. Ed.* 15: 649-652.
- (4) CLIFFORD, P. A. 1943 Report on lead, dithizone method and its interferences. *Jour. Assoc. Off. Agr. Chem.* 25: 385-392.
- (5) COWLING, H., AND MILLER, E. J. 1941 Determination of small amounts of zinc in plant materials. *Indus. and Engin. Chem., Analyt. Ed.* 13: 145-149.
- (6) CRONHEIM, G. 1942 Orthonitrosophenol as a new reagent in colorimetric analysis, determination of cobalt. *Indus. and Engin. Chem., Analyt. Ed.* 14: 445-447.
- (7) ELLIS, G. H., AND THOMPSON, J. F. Nitroso cresol method for determination of cobalt in biological material. *Indus. and Engin. Chem., Analyt. Ed.* (In press).
- (8) GREENLEAF, C. A. 1942 The determination of copper in foods. *Jour. Assoc. Off. Agr. Chem.* 25: 385-392.
- (9) WICHMANN, H. J. 1939 Isolation and determination of traces of metals. The dithizone system. *Indus. and Engin. Chem., Analyt. Ed.* 11: 66-72.

DETERMINATION OF TOTAL AND AVAILABLE BORON IN SOILS¹

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Boron exists in many soils largely as tourmaline, a boroaluminum silicate of great insolubility and resistance to weathering. Some boron, of varying degree of availability, is also present in combination with the organic matter of soils, and probably as salts of calcium and calcium aluminum silicates. In the soils of the arid and semiarid regions, small amounts may be present as salts of sodium.

The procedures which follow for the determination of total and available boron in soils have been used extensively in recent years by a considerable number of investigators. For detailed discussions regarding their use and advantages, the reader is referred to publications by some of these investigators (1-7, 9).

The procedures utilize the quinalizarin color reaction for the final measurement of the boron. If desired, the color reaction with curcumin, as described by Naftel (8), may be applied at the point in the procedures where the quinalizarin solution is added.

PREPARATION OF REAGENTS

Quinalizarin-sulfuric acid solution (98 per cent by weight H_2SO_4 containing 5 mgm. of quinalizarin per liter). Although the strength of the sulfuric acid in this solution may vary from 97.5 to 98.5 per cent by weight, it must be kept within these limits for the determination of small amounts of boron. This requires very careful preparation, storage, and use. The acid is prepared by mixing ordinary c.p. concentrated sulfuric acid with fuming sulfuric acid. To facilitate the calculations involved in determining the proportion of each to be mixed, strengths are expressed in terms of sulfur trioxide rather than sulfuric acid. Accordingly, the desired 98 per cent sulfuric acid becomes 80.0 per cent sulfur trioxide. The proportion of each to be mixed varies, of course, with the strengths of the acids. The concentrated acid usually contains about 95 per cent of sulfuric acid by weight; and the fuming, 20 to 30 per cent of free sulfur trioxide. The exact strength must be determined for each lot used, because the variation is often great enough to cause serious errors. To determine the strength, weigh out 2 or more gm. of the acid into a 25-cc. weighing bottle, and after diluting, titrate with 1.0 *N* sodium hydroxide. Place the weighing bottle containing the concentrated sulfuric acid in a beaker of water, mix, and titrate the acid. Drop the weighing bottle containing the fuming acid into a second 100-cc. weighing bottle containing about 30 cc. of water. As the bottle is dropped, remove the cover of the 25-cc. bottle, and then quickly replace the cover of the larger bottle. After allowing the two weighing bottles to stand overnight or until fuming has entirely ceased, place them with covers removed in a liter beaker containing 300 to 400 cc. of water. Place the cover of the larger bottle in the beaker also, to recover any acid which might be on it. After mixing,

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titrate the acid. Calculate the strengths in terms of sulfur trioxide by means of the following formula:

$$\frac{\text{cc. NaOH titration} \times \text{normality} \times 0.04003}{\text{weight of concentrated or fuming H}_2\text{SO}_4} \times 100 = \text{percentage by weight of SO}_3 \text{ in each case}$$

After determining the strengths of the acids in terms of sulfur trioxide, calculate the proportion of each to be mixed to make 100 gm. of 98 per cent sulfuric acid, equivalent to 80.0 per cent of sulfur trioxide, as follows:

Let x = grams of concentrated sulfuric acid needed

$100 - x$ = grams of fuming sulfuric acid needed

a = strength of concentrated sulfuric acid in terms of sulfur trioxide expressed decimally

b = strength of fuming sulfuric acid in terms of sulfur trioxide expressed decimally.

Then, $ax + b(100 - x) = 80.0$. Solve for x .

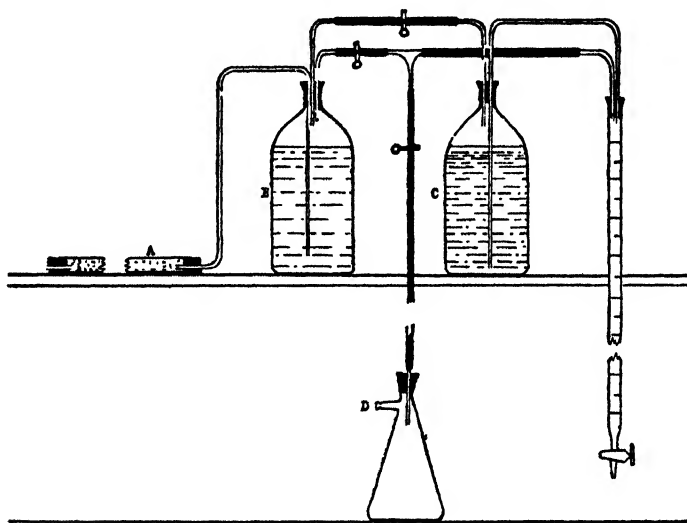


FIG. 1. APPARATUS FOR STORING AND DELIVERING QUINALIZARIN-SULFURIC ACID SOLUTION SO AS TO PREVENT ABSORPTION OF WATER FROM THE AIR

A, Tube containing anhydrous CaCl_2 ; B, Bottle containing 98 per cent by weight H_2SO_4 ; C, Bottle containing quinalizarin-sulfuric acid solution; and D, Suction flask. To fill burette, apply suction at D and release lower and upper clamps. To dispense solution from burette, release middle clamp.

For example: Strength of concentrated sulfuric acid found by titration was 77.78 per cent sulfur trioxide. Strength of fuming sulfuric acid found by titration was 87.41 per cent sulfur trioxide. Substituting these values in the formula above and solving for x :

$$0.7778x + 0.8741(100 - x) = 80.0$$

$$0.0963x = 7.41$$

$$x = 76.9, \text{ grams of concentrated acid needed}$$

$$100 - 76.9 = 23.1, \text{ grams of fuming acid needed in making 100 gm. of desired mixture containing 98.0 per cent H}_2\text{SO}_4.$$

To each liter of 98 per cent sulfuric acid thus prepared, add 5 mgm. of quinalizarin and mix thoroughly to dissolve. Store in a tightly stoppered glass bottle to prevent change in acid concentration, or better, in accordance with the apparatus illustrated in figure 1, which obviates contact with moist air during storage and facilitates accurate dispensing.

Sulfuric acid, approximately 0.36 N. Dilute 5 cc. of 95 to 96 per cent by weight sulfuric acid to 500 cc. with distilled water.

Sulfuric acid, approximately 4 N. Dilute 50 cc. of 95 to 96 per cent by weight sulfuric acid to 450 cc. with distilled water.

Calcium hydroxide, saturated solution. Add 5 to 10 gm. of calcium hydroxide to 500 cc. of distilled water. Shake well and allow to settle.

Potassium carbonate solution. Dissolve 40 gm. of anhydrous potassium carbonate in 100 cc. of distilled water. Five drops of this contains about 0.1 gm. of potassium carbonate.

Standard boric acid solutions. Dissolve 2.8578 gm. of c.p. boric acid in 1,000 cc. of distilled water. This solution contains 0.5 mgm. of boron per cubic centimeter and serves as the primary (A) base stock solution. Prepare a second (B) stock solution containing 0.01 mgm. of boron per cubic centimeter by diluting 20 cc. of the primary base stock solution to 1,000 cc. with distilled water, and a third (C) stock solution containing 0.001 mgm. of boron per cubic centimeter by diluting 100 cc. of the second stock solution to 1,000 cc.

PREPARATION AND USE OF COLOR STANDARDS

The colorimetric readings may be made satisfactorily by either photoelectric means or visual observation. In either case, it is necessary to prepare a set of color standards, using known amounts of boron.

When the photoelectric procedure is followed, the color standards are used for obtaining colorimetric readings which serve in making a standard or reference curve, after which the color standards are needed only to check constancy of conditions from time to time. The volume of color standard needed will vary with the type of colorimeter used.

With the Evelyn photoelectric colorimeter, ordinary but selected 7-inch by $\frac{7}{8}$ -inch test tubes are used to hold the standard color solution, of which a volume of 10 cc. is adequate. Obviously these tubes must be made of boron-free glass. The high refractive index of the concentrated H_2SO_4 color solution tends to magnify greatly the influence on light transmittance of any small defects or scratches on the comparison tubes. It was found that the best method of selecting a satisfactory set of comparison tubes is to place about 15 cc. of the color solution (the solution of previous tests may be used) in each tube and determine the scale readings of the colorimeter for each tube when a 620 filter is used. Tubes are then selected which give practically the same reading. In many cases the reading changes with a change in orientation of the tube. If tubes showing this characteristic are to be used, it is necessary, by means of a suitable mark, to maintain the same orientation during all readings. Slight variations in tubes may be compensated for by using a correction factor. All tubes should be checked frequently, because any slight scratching or marring that results from handling may seriously influence the transmission of light. The outside of the tubes should be perfectly clean and relatively free of condensed moisture when readings are made.

Also, in the case of the Evelyn instrument, the color filter No. 620 (595 to 660 $\text{m}\mu$ transmittance) gives the greatest range in scale readings and is, therefore, used.

When the colorimetric readings are made by visual observation, it is convenient and satisfactory to use glass vials, approximately 20- by 100-mm., rather than test tubes, as containers of the standard and unknown color solutions, because the vials have flat bottoms which facilitate their use.

For the preparation of a set of standard color solutions, add by means of burettes the following volumes of stock solution, B or C, and distilled water to a set of test tubes or vials:

NO.	BORON STOCK SOLUTION B OR C	DISTILLED WATER	BORON PRESENT
	cc.	cc.	mgm.
1	0.00	1.00	0.0000
2	0.20 (C)	0.80	0.0002
3	0.40 (C)	0.60	0.0004
4	0.60 (C)	0.40	0.0006
5	0.80 (C)	0.20	0.0008
6	1.00 (C)	0.00	0.0010
7	0.15 (B)	0.85	0.0015
8	0.20 (B)	0.80	0.0020
9	0.25 (B)	0.75	0.0025
10	0.30 (B)	0.70	0.0030
11	0.35 (B)	0.65	0.0035
12	0.40 (B)	0.60	0.0040

Next, add 10 cc. of the quinalizarin-sulfuric acid solution. Stopper the vials or test tubes and cool to 25° C., after which the standards are ready for use.

DETERMINATION OF TOTAL BORON

The procedure for total boron in soils departs only slightly from that given in the original report (1). McHargue and Hodgkiss (6), using essentially this procedure, which involves fusion with sodium carbonate, report satisfactory results in the determination of total boron in soils.

In determining the total boron content of soils by means of the fusion method, it is necessary to use a high proportion of sodium carbonate to soil. Treatment of the melt obtained with water alone will bring all the boron into solution, but this method is inconvenient because of its slowness and the large quantity of water required. Addition of sulfuric acid, to the water, so that the final reaction of the solution falls within the pH range of 5.5 to 6, hastens the disintegration of the melt and leaves most of the sesquioxides and silica in insoluble form. Addition of alcohol up to 60 or 70 per cent by volume at this point serves to throw down most of the large amount of sodium sulfate that has been formed. This leaves all the boron and only a small amount of salts in solution. After the final evaporation, ignition is necessary because of the small amount of nonvolatile organic matter usually introduced with the alcohol.

Analytical procedure. Weigh out a 0.5-gm. sample of the soil (100-mesh); then put 3 gm. of anhydrous Na_2CO_3 in a platinum crucible, place the soil sample on top of the Na_2CO_3 , and mix the two thoroughly with a glass rod. Level off the charge and brush off the rod. Place the crucible on a nichrome triangle in a slightly inclined position and adjust the cover so as to leave the crucible about one-eighth open to prevent reducing conditions. Heat over a low flame for 5 to 10 minutes so that the bottom of the crucible takes on a dull redness. This low heating drives out moisture gradually and thus prevents spattering. Now, gradually increase the heat so that after 5 to 10 minutes more, the mass completely fuses and forms a liquid melt. The cover should be kept adjusted so that the crucible is partly open. Do not envelope this opening with the flame, as that will prevent access of oxygen to the contents of the crucible.

When bubbles of gas cease to come off, fusion is complete. To ensure fusion of any material sticking on the upper sides of the crucible, incline the crucible so that the main fused mass covers it, and while in this position, heat until the material fuses with the main mass. When fusion is complete, grasp the crucible with the tongs and give it a rotary motion so as to spread the contents over the sides of the lower half of the crucible, thus expediting subsequent removal and solution.

After cooling, place the crucible in a 250-cc. beaker containing about 50 cc. of distilled water. Put a cover glass on the beaker and add 4 or 5 cc. of approximately 4 *N* sulfuric acid from time to time until the melt has disintegrated and the solution, as revealed by means of a spot-plate test with a suitable indicator, has a reaction in the range of pH 5.5 to 6.0. Transfer the solution to a 500-cc. volumetric flask. Wash the beaker and crucible several times with distilled water and add the washings to the flask. The total volume of solution now should not exceed 150 cc. Add methyl or ethyl alcohol to the flask until a volume of 500 cc. is reached, and mix the contents thoroughly, after which, filter or centrifuge to obtain a clear extract.

Place a 400-cc. aliquot of the clear extract in a 500-cc. beaker (boron-free glass) and add 100 to 150 cc. of distilled water to prevent subsequent early precipitation. Add potassium carbonate until the solution is alkaline, evaporate to a small volume, and transfer to a platinum dish. Evaporate to dryness and ignite just enough to destroy organic matter. After cooling, add 4 cc. of approximately 0.36 *N* sulfuric acid, and triturate thoroughly with a policeman. Place a 1-cc. aliquot of this solution (representing 0.1 gm. of soil) in a comparison vial or test tube, add 10 cc. of the quinalizarin-sulfuric acid solution, stopper the tube, and mix thoroughly by whirling gently. Cool to 25° C. or other desired temperature and then make color readings with a set of standards or by means of the photoelectric colorimeter. The final visual comparison is best made by removing the stoppers momentarily from the tubes and making a vertical observation against a white background, as is usually done in colorimetric comparisons.

Report results in parts per million of dry soil. Sandy soils often contain only several parts of boron per million parts of soil; the heavier and better soils often contain 25 to 75 parts.

DETERMINATION OF AVAILABLE BORON

The available boron of soils is, for the most part, water-soluble. It was found (1) that when a known amount of soluble boron in the form of boric acid was added to several soils free of water-soluble boron, and the soils were then dried, the added boron could be completely recovered by adding water, boiling for 5 minutes, and then filtering. The addition of hot water followed by shaking for 30 minutes and then filtering did not result in complete recovery. Complete recovery may be effected by extraction with dilute acid; this procedure, however, raises complications with calcareous soils because of the difficulty of regulating the acidity. Furthermore, tests made with acid extractions of calcareous soils indicated that the results thus obtained often do not correlate well with crop indications of the boron status. After numerous tests, refluxing of the soil-water suspension for 5 minutes appeared to be the best procedure. More boron was extracted by refluxing for 5 to 10 minutes than for shorter or for longer periods. Boiling with a reflux condenser keeps the volume constant, and thus an aliquot is taken more easily later. It was shown (2) that the results thus obtained correlate well with plant response to boron fertilization. De Turk and Olson (4) indicate that water-soluble boron is a fairly reliable measure of the available boron content of soils.

Analytical procedure. Place a 20-gm. sample of the soil (air-dried, 20-mesh) in a 125-cc. Florence flask (boron-free glass), add 40 cc. of distilled water, and then attach a reflux condenser. Boil for 5 minutes, disconnect the condenser, and filter the suspension with suction on a Büchner funnel, or centrifuge until the supernatant liquid is clear. Clarification may be facilitated by adding not more than 0.05 gm. $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Place 20 cc. of the clear extract in a platinum dish and add 5 drops of the K_2CO_3 solution, or place in a porcelain crucible and add 2 cc. of a saturated solution of $\text{Ca}(\text{OH})_2$. Evaporate to dryness and ignite gently to destroy nitrates and all organic matter. After cooling, add 5 cc. of the approximately 0.36 N H_2SO_4 and triturate thoroughly with a policeman. Filter through a 9-cm. paper; by means of a 1-cc. pipette, place *exactly* 1 cc. of the filtrate (representing 2 gm. of soil) in a comparison vial or test tube; then add exactly 10 cc. of the quinalizarin-sulfuric acid solution, stopper the vial or tube, and mix thoroughly by whirling gently. Cool to 25° C. or other desired temperature, and make color readings exactly as for total boron.

Report results in terms of parts per million of available boron in the dry soil. The content usually varies from less than one to several parts; beets require at least 1 p.p.m., many garden and truck crops slightly less, and general farm crops usually not more than 0.5.

PRECAUTIONS

Since many chemicals commonly used contain appreciable amounts of boron, it is essential that all chemicals used in the determination of boron be tested for freedom from this element. Ordinary Pyrex glass contains about 11 per cent of boric oxide and may cause serious contamination if used in this determination. All liquid reagents should be stored in containers made of boron-free glass. Common soft-glass bottles are usually satisfactory. Slight imperfections in the glass of the color comparison vessels or the presence of small amounts of foreign matter on the surface of these vessels may cause serious errors in the photoelectric color readings.

Great care must be exercised in measuring the 1-cc. aliquot of the unknown test solution to which are added the reagents for color development, because an error of 1 drop in this measurement may cause an error of 5 to 10 per cent in the final result through its influence on the final acid concentration in the mixture. Contact of the quinalizarin-sulfuric acid solution with moist air should be scrupulously avoided both before and after the reagent is dispensed.

REFERENCES

- (1) BERGER, K. C., AND TRUOG, E. 1939 Boron determination in soils and plants using the quinalizarin reaction. *Indus. and Engin. Chem., Analyt. Ed.*, 11: 540-545.
- (2) BERGER, K. C., AND TRUOG, E. 1940 Boron deficiencies as revealed by plant and soil tests. *Jour. Amer. Soc. Agron.* 32: 297-301.
- (3) BERGER, K. C., AND TRUOG, E. 1943 Boron tests and determination for soils and plants. *Soil Sci.* 57: 25-36.
- (4) DE TURK, E. E., AND OLSON, L. C. 1941 Determination of boron in some soils of Illinois and Georgia. *Soil Sci.* 52: 351-357.
- (5) MCHARGUE, J. S., AND HODGKISS, W. S. 1941 Report on less common metals in soils. *Jour. Assoc. Off. Agr. Chem.* 24: 250-252.
- (6) MCHARGUE, J. S., AND HODGKISS, W. S. 1942 Report on boron and fluorine in soils. *Jour. Assoc. Off. Agr. Chem.* 25: 311-313.
- (7) MAUNSELL, P. W. 1940 The estimation of boron by means of quinalizarin. *New Zeal. Jour. Sci. and Technol.* 22: 100B-111B.
- (8) NAFTEL, J. A. 1939 Colorimetric microdetermination of boron. *Indus. and Engin. Chem., Analyt. Ed.* 11: 407-409.
- (9) OLSON, L. C., AND DE TURK, E. E. 1940 Rapid microdetermination of boron by means of quinalizarin and a photoelectric colorimeter. *Soil Sci.* 50: 257-264.

DETERMINATION OF VANADIUM AND MOLYBDENUM IN SOILS

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The most successful method for the determination of vanadium and molybdenum in soils is that of Sandell.²

The soil sample should be ground to pass a 100-mesh sieve. For the determination, take 2 to 5 gm., according to whether the soil is clayey or sandy, and ignite in an oxidizing atmosphere in a suitably large platinum crucible to destroy organic matter. Thoroughly mix the residue with five times its weight of c.p. sodium carbonate and heat, gently at first, finally for $\frac{1}{2}$ hour, over a good burner of the Fisher type. Swirl the crucible during cooling so as to solidify the melt largely on the sides. Cool on a cold slab of iron to shrink the crucible and gently press and roll the inverted crucible over a 250-cc. beaker. The melt should detach easily and fall into the crucible. Add about 100 cc. water and a few drops of ethanol, and heat on a steam bath until the melt is disintegrated. Rinse the crucible and cover into the beaker, and filter into a 200-cc. volumetric flask. The filter paper should have been washed with a hot solution of sodium carbonate to remove any coloring matter present. A yellow color of the filtrate shows the presence of chromium, which may be determined colorimetrically if desired.

VANADIUM

Reagents

Special solutions are prepared as follows:

8-Hydroxyquinoline, 2.5 per cent. Dissolve 2.5 gm. finely powered 8-hydroxyquinoline in 100 ml. of 2 *N* acetic acid.

Sodium tungstate, 5 per cent. Dissolve 5 gm. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (reagent quality) in 100 ml. water.

Standard vanadium solution. Prepare a solution of ammonium metavanadate (or other alkali vanadate) containing 0.01 mgm. V_2O_5 per milliliter by diluting a stronger solution. Standardize the stronger solution in the usual manner by reducing the acid solution with SO_2 and titrating with standard permanganate after expulsion of SO_2 .

Procedure

For the determination of vanadium take an aliquot corresponding to 0.5 to 2 gm. soil, depending on the probable vanadium content. Transfer to a small Erlenmeyer flask and add 1 drop methyl orange indicator solution. Add 4 *N* H_2SO_4 from a burette till the solution assumes the intermediate color of the indicator. Swirl the liquid to liberate carbon dioxide and transfer the solution to a small separatory funnel. Add 2 ml. chloroform (reagent quality) and 0.1 ml. 8-hydroxyquinoline solution. Shake moderately vigorously for 1 minute, allow the layers to separate, and draw off the chloroform into a platinum crucible; add 1 ml. chloroform to wash out stem of funnel. Then add 2 ml. chloroform and 1 ml. 8-hydroxyquinoline, shake as before, and transfer the chloroform to the platinum crucible. Repeat the extraction once more with chloroform and 8-hydroxyquinoline. A total of three extractions should suffice for most of the samples. The last extraction should show only a faint yellowish coloration due to the 8-hydroxyquinoline itself. Add 0.1 gm. Na_2CO_3 to the crucible containing the extract, and evaporate to dryness at a low temperature. Heat the crucible in a flame to destroy organic matter then at the full heat of the burner for 1-2 minutes. Cool, dissolve in 3-4 ml. H_2O , and transfer the solution to a color comparison tube. It is convenient to use a tube having a diameter of 1.5 cm. and a length of 15-16 cm. If the vanadium content of the sample is very small (less than 0.005 per cent V_2O_5) it is preferable to use a narrow tube to increase the precision of the color

¹ Bureau of Plant Industry, Soils, and Agricultural Engineering.

² *Indus. and Engin. Chem., Analyt. Ed.* 8: 336, 1936.

comparison. Rinse out the crucible with one or two portions of water of several milliliters each so that the total volume of the solution will be 8–10 ml. The solution should be colorless and free from any turbidity; if the solution is appreciably turbid, filter it through sintered glass or porcelain filter crucible, not through paper.

To a second identical tube add 0.1 gm. Na_2CO_3 and a few milliliters less water than in the first tube. Then add the following, in succession, to both tubes and mixing after each addition: 1 ml. *N* sulfuric acid (free from reducing substances), 0.1 ml. 85 per cent phosphoric acid, and 0.2 ml. sodium tungstate solution. Add the standard vanadium solution to the comparison tube, until, after mixing, the colors of the two solutions match when the tubes are viewed axially against a white background. Near the end point, water should be added to the solution having the lesser volume until both tubes contain approximately the same volume of liquid.

MOLYBDENUM

Reagents

Special solutions are prepared as follows:

Potassium thiocyanate, 5 per cent.

Stannous chloride, 10 gm. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 ml. 1:9 HCl. This solution should be freshly prepared.

Standard molybdate solution, 0.05 mgm. MoO_3 per milliliter, prepared by diluting an ammonium molybdate solution 10 or 20 times as strong. Obtain the exact strength of the strong solution by precipitating as lead molybdate.

Ethyl ether, treated with thiocyanate and stannous chloride. Shake reagent quality ether with one-tenth its volume of a mixture of equal amounts of potassium thiocyanate and stannous chloride solutions the same day it is to be used.

Standard molybdenum thiocyanate solution. Transfer 5 ml. of the standard ammonium molybdate solution and 50 ml. of a 5 per cent sodium carbonate solution to a separatory funnel, add carefully 8 ml. concentrated HCl, swirl to liberate CO_2 , and cool to 20°C . Then add 3 ml. each of potassium thiocyanate and stannous chloride, in the order named, mixing well after each addition. After 30–45 seconds extract with 10 ml. ether and run the latter into a dry 25-ml. volumetric flask. Extract with several small portions of ether until the last extract is nearly colorless, and make the volume up to 25 ml. There is thus obtained a solution containing an equivalent of 0.01 mgm. of MoO_3 per milliliter. Great care should be taken to prevent changes in concentration as a result of evaporation. Transfer the solution to the microburette rapidly and keep the latter well covered. Because of its instability, the solution cannot be kept longer than a day.

Transfer an aliquot of the sodium carbonate solution of the soil corresponding to 1 to 4 gm. of the soil to a separatory funnel of suitable size and add slowly and with agitation 8 cc. concentrated HCl for every 2.5 gm. of Na_2CO_3 used for the aliquot, swirl to liberate CO_2 , and cool to 20° . Add 5 ml. of the thiocyanate solution, mix, and add an equal volume of the stannous chloride solution; after mixing allow to stand 30 to 45 seconds. Add 10 cc. reagent quality ether to the funnel, shake vigorously for 30 seconds, allow the liquids to separate, draw off the aqueous layer into a beaker, and run the ether into a color comparison tube having a diameter of approximately 10 mm. Return the aqueous solution to the funnel, extract with 2–3 ml. ether and add it to the first extract in the comparison tube.

To make the color comparison, add the standard ethereal solution of molybdenum thiocyanate from a microburette to a second identical tube containing an appropriate volume of ether, treated with thiocyanate and stannous chloride, until the colors match, when viewed from above against a white background. Run a blank on the sodium carbonate used through all the steps of the procedure.

WATER-SOLUBLE VANADIUM AND MOLYBDENUM

If it is desired to estimate water-soluble vanadium and molybdenum, the solutions containing these elements may be evaporated to dryness, the residue ignited with sodium carbonate, and the determinations carried out as above.

DETERMINATION OF TOTAL SELENIUM AND ARSENIC IN SOILS

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SELENIUM

Selenium and arsenic are quantitatively distilled as bromides from strong hydrobromic acid solutions. The distillation process is well adapted to soils, as it separates extremely small quantities of these elements from large masses of soils. The method for selenium is probably as sensitive as any simple chemical method known in soil analysis. With the integration process described below it is possible to detect with certainty as little as 1 part of selenium in 10 billion parts of soil.

Procedure

Place 50 gm. of a 2-mm. soil sample in a distilling flask equipped with a short condenser and thistle safety tube. The apparatus should have all glass ground connections to prevent contamination by rubber (fig. 1). Add 100 cc. HBr to which has been added 2 cc. Br, warm gently for 15 minutes, and distill into a 100-cc. Erlenmeyer flask containing 5 cc. H₂O. Have the outlet of the distilling tube submerged. If, on gentle warming, a drop of bromine does not collect beneath the H₂O in the receiver, add 2 cc. Br to the distilling flask through the thistle tube and repeat the gentle warming. Distill 60 cc. into the receiver. To the distillate in the Erlenmeyer add 25 cc. H₂O, and cool in ice water. Pass a slow stream of SO₂ into the distillate until the Br disappears. Add 0.25 gm. hydroxylamine hydrochloride (NH₂OH·HCl). Warm the Erlenmeyer on a steam bath at 80°C. for 15 minutes and allow to stand overnight. The selenium (element) will appear on the bottom as a rose-pink precipitate. Modify the further treatment according to the quantity of precipitate as directed below.

Precipitate not greater than 0.5 mgm. Filter Se precipitate through asbestos on a small Gooch crucible. If oily particles are present, wash asbestos pad with 10 cc. alcohol and then with 10 cc. H₂O. Dissolve the precipitated Se from the pad with 10 cc. 48 per cent HBr which has been colored bright red by added Br, and wash by suction into a 25-cc. volumetric flask with 2 portions of H₂O. Decolorize filtered solution with SO₂ and add 1 cc. solution containing 100 mgm. NH₂OH·HCl and 25 mgm. gum arabic. Make up to volume with H₂O, warm flask and contents on steam bath at 80° for 30 minutes, cool to room temperature, shake vigorously and transfer to a 50-cc. Nessler jar. Before this final precipitation, prepare a series of standards, in 25-cc. volumetric flasks, of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 0.7 mgm. Se as Na₂SeO₃ and treat them precisely as sample is treated. Compare in any suitable color comparator, and report results as parts per million on air-dried soil.

Se below 1 p.p.m. as determined previously. Distill 100 gm. with HBr as above. When distillation is complete, wash out flask and place another 100-gm. sample of soil in the distilling flask, add the distillate from the first sample plus 50 ml. additional HBr, 2-4 ml. Br and 22 ml. H₂SO₄, mix and distill as before. Repeat the operation with as much soil as is necessary to integrate a measurable quantity of selenium.

Se in excess of 0.5 mgm. Dissolve the precipitate in the HBr + Br mixture and transfer the dissolved material to a 100-ml. beaker, dilute with 20 per cent HBr to a volume

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of 50 ml. Precipitate this solution with SO_2 and add 0.25 gm. $\text{NH}_4\text{OH}\cdot\text{HCl}$, warm on steam bath for 15 minutes and allow to stand overnight. Filter on a weighed Gooch, dry 4 hours at 85°C ., and weigh.

The quantity of selenium isolated by the distillation may be titrated with $\text{Na}_2\text{S}_2\text{O}_3$ instead of using the turbidimetric method.³

ARSENIC

Arsenic is distilled quantitatively and accompanies the selenium as distilled above. Selenium need not be separated for the arsenic determination, but if selenium is determined, arsenic may be determined in the filtrate from the selenium precipitation. For the arsenic determination separately, it is not neces-

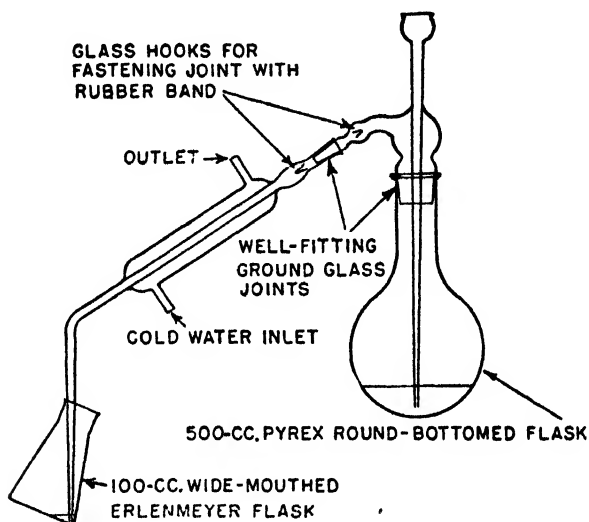


FIG. 1. APPARATUS FOR DETERMINING SELENIUM IN SOILS

sary to use so much soil: 10 gm. is ample. Proportionately small quantities of the reagents may be used.

Reagents. (a) Dissolve 25 gm. ammonium molybdate in 200 ml. H_2O heated to not more than 60°C . Dilute 280 cc. H_2SO_4 (free from arsenic and phosphorus) to 800 ml. When cool, add the molybdate to the acid solution, slowly, with stirring, and make up to 1 liter. (b) Dissolve 2.5 gm. stannous chloride in 100 ml. dilute HCl (1:10). Preserve under white mineral oil.

Procedure. Use the distillate from 10 gm. soil or an aliquot of the selenium filtrate corresponding to 10 gm. soil. Add the distillate containing the arsenic in several portions to a casserole, containing an excess of nitric acid, on the steam bath. The bromine from each portion should be nearly expelled before the next portion is added. When evaporation is complete, wash down the sides of the casserole and repeat the evaporation. Estimate

³ Association Official Agricultural Chemists 1940 Official and Tentative Methods of Analysis, ed. 5, pp. 417-418. Washington, D. C.

the arsenic content by the method of Truog and Meyer.³ To do this, dissolve the arsenic residue in water and transfer to a 50-cc. volumetric flask and add 2 ml. of the ammonium molybdate reagent (a) and exactly 3 drops of stannous chloride solution (b), mix thoroughly, and allow to stand 10 minutes. Compare in a suitable colorimeter with standards similarly treated and of approximately the same depth of color. Standards must be prepared with each set of samples as the color developed is not permanent. If the arsenic determination is made on the filtrate from the selenium determination it is necessary to neutralize the sulfuric acid formed by sodium hydroxide after the evaporation of the excess nitric acid.

WATER-SOLUBLE SELENIUM AND ARSENIC

If water-soluble selenium and arsenic are to be estimated the solution may be treated with sufficient Na_2O_2 in the cold and evaporated to 50 ml. or less and distilled with hydrobromic acid as above. In rare cases it may not be necessary to distill, but in most cases, the presence of salts or organic matter make the distillation necessary. The distillation process separates the arsenic from interfering phosphorus.

³ *Indus. and Engin. Chem., Analyt. Ed.* 1: 136-139, 1929.

SOIL REACTION—GLASS ELECTRODE AND COLORIMETRIC METHODS FOR DETERMINING pH VALUES OF SOILS¹

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Sorensen defined pH as the negative logarithm of the hydrogen-ion concentration of a solution. A pH measurement of a soil, however, is at best an approximation. One is dealing with a multiphase system of water and solid soil particles, which may be more or less in equilibrium with a gaseous phase. The system is not homogeneous throughout, in the sense of the homogeneity of true solutions. The principal source of active hydrogen ions is in the surface of the solid soil particles. The soil colloidal matter behaves very much as a weak acid or a mixture of a weak acid and salt of that acid. The hydrogen ions in solution are in equilibrium with those particles. The value obtained in the measurement of soil pH would therefore be affected somewhat by any manipulation which influences the extent and intimacy with which the indicator dye or electrode comes in contact with the colloidal soil particles. These will be discussed in more detail in this paper.

Methods of determination of soil reaction may be divided roughly into two classes, electrometric and colorimetric.

ELECTROMETRIC METHODS

In the electrometric methods an electrode the potential of which is a direct function of hydrogen-ion concentration is immersed in a solution or suspension, connected with another standard half-cell (usually the calomel) and the electromotive force of the cell is measured potentiometrically. Four general types of electrodes have been used for this purpose; namely, the antimony, hydrogen gas, quinhydrone, and glass electrodes.

The antimony electrode has never found widespread use in soil pH measurements. The hydrogen electrode was at one time the standard but was largely replaced by the quinhydrone in the early 1920's chiefly because of its greater convenience. The quinhydrone electrode, an oxidation-reduction electrode, was not applicable above pH 8.5 because of the dissociation of the hydroquinone component. Furthermore, it can not be used in the presence of oxidizing and reducing constituents which affect the state of oxidation of the quinone or hydroquinone. Reducing constituents in waterlogged soils and manganese dioxide in many soils were found to introduce rather serious errors and are so common as to limit the usefulness of this electrode.

Within the past few years the glass electrode has largely replaced other electrodes for measuring soil pH values. The details of the glass electrode are

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thoroughly discussed by Dole (8). This electrode is not influenced by oxidizing or reducing substances, can be used satisfactorily over the entire range of pH commonly encountered in soils, and is subject to negligible salt errors under conditions encountered in most soils. Its high electrical resistance limited its usefulness for some time. Electrodes were made thin so as to keep resistance low enough to measure potentials with available equipment. As a result of recent advances in the development of electronic amplifiers, this difficulty has been largely overcome and relatively sturdy electrodes can be used satisfactorily.

A number of commercial instruments for measuring pH with the glass electrode are available and operate very satisfactorily. The electrode has a small inconstant asymmetry potential and consequently must be standardized at intervals against stable buffer solutions. Viebel's buffer (0.01 *N* HCl and 0.09 *N* KCl) pH 2.03; 0.05 *M* potassium acid phthalate, pH 3.97; and a phosphate buffer with a pH about 7.00 are convenient as reference standards.

Results should be reported as pH values. Although measurements are often reproducible to 0.01 or 0.02 pH, it is doubtful whether anything is gained by reporting measurements on field soils any closer than to the nearest 0.1 pH.

COLORIMETRIC METHODS

Although the electrometric method constitutes the most accurate measurement of the pH value of soils, colorimetric methods have a place where a laboratory or individual cannot afford the cost of an electrometric assembly and where the use to be made of the values does not necessitate a high degree of accuracy. This is very often the case in estimating lime requirement.

Snyder (23) has reviewed the procedures, as well as the principles embodied in many of the colorimetric methods in use to any extent. Pierre (20) has found colorimetric methods convenient and accurate for determining the pH of filtered soil extracts and soil solutions, provided certain precautions are observed. Wilcox (25) studied the pH of displaced soil solutions and suggested that the lowest ratio of water to soil should be used in the use of extractions for pH determination.

Various methods involved the separation of a clear extract for determining pH value, and direct contact of soil with the indicator. In the former, the different methods make use of centrifuging, filtration, flocculation, or dialysis for obtaining the clear extracts. The pH is determined by comparison with a color chart or with standards using some type of comparator.

A number of different commercial sets have been designed for colorimetric determination of soil pH.

Mason and Obenshain (19) compared a number of such colorimetric methods on 150 soil samples representative of the soils of Virginia. Determinations of pH were also made by means of the hydrogen, glass, and quinhydrone electrodes. The results showed that of the colorimetric methods tried the LaMotte-Hester and the Hellige methods were most accurate. These methods involve the use of barium sulfate as a flocculating agent and the treatment of an aliquot of the soil extract with a given quantity of indicator solution. As compared with

hydrogen electrode determinations of pH, in no case was the deviation more than 0.3 unit, and in 90 per cent of the soils it did not exceed 0.2 pH unit. For field use or where the facilities for operation of the LaMotte-Hester method were not available, the modified Indiana method or the LaMotte-Morgan method was reasonably satisfactory. These are methods in which there is direct contact of the soil with the indicator solution. In over 90 per cent of the soils, the deviation from the standard was less than 0.4 pH.

The use of one of these colorimetric methods for pH determination could be helpful where electrometric methods are impractical and where a range of 0.2 to 0.3 unit in pH is accurate enough to be of use.

FACTORS AFFECTING THE pH VALUE OF SOILS

The pH value of soils is affected by various factors. For example, dilution or aspiration may influence the extent to which the indicator dye or electrode comes into contact with the colloidal soil particles; or it may affect the relative pressure of CO₂ or the concentration of salts in true solution. Other factors such as drying and periodic variation have been investigated. Although the effect of these various factors on the values obtained will be discussed separately, their interrelationships are recognized.

Effect of dilution (soil : water ratio)

Earlier work on the effect of soil:water ratio has been reviewed by Snyder (23). Until recently, soil-water ratios of 1:2 to 1:5 have been most widely used for air-dried mineral soils. A ratio of 1:2.5 was adopted by the International Society of Soil Science in 1930. Such ratios give a dilution which does not represent conditions as they normally occur in the field. Keaton (13) points out that these higher dilutions have been used both because of the type of apparatus for measuring H-ion concentration and because of the reproducibility of the pH value at higher dilutions. McGeorge (15) showed the desirability of determining pH of the soil at field moisture contents and proposed the use of a spear-type glass electrode. Since then, other workers, particularly Haas (10), Huberty and Haas (12), Chapman *et al.* (5), and Davis (7), have used the glass electrode extensively in field and laboratory studies of soils with low moisture contents. With the development of the glass electrode, it has been generally assumed that the mechanical and technological difficulties of such determinations have been largely eliminated. In dry soils, however, Davis (7) has shown that commercial vacuum tube amplifiers may give erroneous results because the product of grid current and resistance of the soil yields an extraneous electromotive force. Davis found also that the apparent pH obtained in soils of low moisture contents depends upon the treatment given to the glass electrode before use. He concludes that it is undesirable to attempt to measure the pH of soils below the moisture equivalent. McGeorge (15) and Chapman *et al.* (5) are in agreement with this idea.

Most recent work indicates, therefore, that the pH value is erratic and unreliable when determinations are made on soils with moisture contents at the

moisture equivalent or below. On the other hand, when the soil-water ratio is 1:2.5 or greater, pH values may be significantly higher than those determined on soil at moisture contents characteristic of probable field conditions. It would seem desirable then to make pH determinations at as low a dilution as is practical. In view of the wide range in clay content, it is not logical to keep the ratio of soil to water constant for all soils. Constant ratios in practice have been dictated by the inconvenience attendant on adjusting the soil:water ratio to any fundamental soil moisture value.

Effect of stirring and aspiration

According to Bailey (2), agitation of the suspension during the determination with the glass electrode is essential for reliable results, especially with coarse-textured soils. The hydrogen ions that may affect the reaction of a soil are not all free, as in the case of a soluble acid, but most of them are held at or near the surface of the soil particles. Hence, in order to measure the intensity or activity of these ions, it is necessary to have the soil in contact with the electrode. Soil suspensions containing large-sized particles or clay in a flocculated condition should be stirred during or just before the measurement is made.

If a pH measurement is made on a solution or soil suspension of low ionic content which is being stirred either mechanically or by aeration, the value obtained is lower than it would be if the liquid were not in motion. The error introduced may be as much as 0.4 pH, although it is usually the order of 0.1 unit.

Agitation should be sufficient to keep the soil material in suspension, and may be obtained by mechanical stirring or by aeration. The use of aeration for stirring, though more desirable, involves the use of some special type of bubbling vessel. A few such vessels have been designed and are reported to be satisfactory, but their distribution is not widespread.

Effect of carbon dioxide

Carbon dioxide is present in variable amounts as a normal constituent of the soil-water system under both laboratory and field conditions. Dissolved carbon dioxide has the effect of lowering the pH value of the system. Since the first dissociation constant of carbonic acid is 3×10^{-7} , the effect on soil reaction is usually small in soils having pH values below 6.0 and usually need not be considered. In slightly acid to alkaline soils, however, the presence of CO_2 may lower the pH value by 2.0 or more units. Whitney and Gardner (24) worked with such soils and found that the pH is approximately a straight-line function of the log of the CO_2 pressure, in the pressure range from about 0.0003 to 1 atmosphere of CO_2 at constant moisture. They conclude that expressing the pH of such soils as variable functions of CO_2 pressure would give a better indication of the probable pH range in the field in the presence of plant roots and biological activity than could be obtained from single pH measurements. Since the pH is apparently a straight-line function of the log of CO_2 pressure, two points would be sufficient to determine a curve at constant moisture. A relatively simple apparatus for the electrometric titration of soil suspensions with carbonated water is described by Gardner and Whitney (9).

It would seem that the decision as to whether the carbon dioxide should be considered when pH measurements are made should be based on the type of soil and on the purpose for which the determination is made. In connection with problems concerning plant growth, if a sample of soil is brought into the laboratory in a moist condition or the measurement is to be made in the field, then the measurement could be made on the moist soil with the carbon dioxide present.

For purposes of characterizing the soil, however, it is desirable that the pH value be reproducible and that it be made under conditions that will eliminate as far as possible the effect of season of the year and biological activity. This may be done by aspiration of a gas with constant CO₂ composition. Ordinary air (0.03 per cent CO₂), CO₂-free air, nitrogen, hydrogen, and others have been used. Agitation with CO₂-free air or other gases has the disadvantage of producing a CO₂ pressure lower than would likely be found in the field and, therefore, giving a pH value higher than the maximum under field conditions.

Periodic variation

The effect of time of sampling on the pH value of the soil has been given much attention. Snyder (23) has reviewed the earlier work concerning fluctuations in pH value of soils throughout the year. Undoubtedly, factors which contribute to variations in the carbon dioxide content are responsible for some of these fluctuations. Drying, nitrification, and differential absorption of cations and anions by plants may also be contributing factors. The seasonal factor is of especial importance on soils with low buffer capacity, according to Hester and Shelton (11). They assert that for truck crops, lime recommendations made on the basis of the pH value of the soil without knowledge of the seasonal variation would lead to considerable error. This fact is further emphasized by Carolus and Lucas (4), who found considerable fluctuation in pH during a year in which the rainfall distribution was such that unusually dry or wet periods occurred. They found, as did Baver (3), that the acidity of the soil increased during extremely dry periods, but usually returned to the higher pH value during wet periods. Other workers have found, on the other hand, that just the opposite occurred. The likelihood of seasonal variation should be kept in mind when making pH determinations for use in connection with problems concerning plant environment.

Effect of drying and grinding

Bailey (1) made a rather extensive study of the effect of air-drying on the hydrogen-ion concentration of the soils of the United States. The most important factor affecting the changes in reaction due to air-drying appeared to be the amount of acid organic matter present in the sample. The greater portion of the samples he studied did not change more than 0.1 pH in any of their horizons on air-drying. He concluded that hydrogen-ion determinations should be made on air-dried soils rather than on samples fresh from the field.

Theoretically, the effect of air-drying should be of greater concern in alkaline soils than in acid soils because of the influence of CO₂ on pH. McGeorge (14)

found that the pH value of alkaline calcareous soils was increased by drying, but that the differences were inappreciable except for the black alkali soils.

In general, it is agreed that air-drying of soils is accompanied by a change in reaction, but the magnitude of the change is usually small. Often it is not feasible to make pH determinations before soil samples become air-dry. Furthermore, drying may be necessary if one is to remove the material larger than 2 mm. in diameter and obtain a representative sample. In such cases it is considered more practical to make all determinations on samples that have been air-dried.

Grinding a soil finely may affect the pH in either the acid or the alkaline direction, depending on the nature of the new mineral matter exposed to solution. The possible effects of grinding have been discussed by Baver (3) and McGeorge (14). The indications are that it is preferable to use the unground sample.

Miscellaneous effects

The use of distilled water is usually recommended for pH determinations on soils. McGeorge (16), however, suggests the use of tap water because its composition is similar to that of the irrigation waters in Arizona. When tap water was used, even black alkali soils showed little change in pH with variation in the soil-water ratio. At best, the use of tap water is a somewhat questionable practice because of the variation in its properties from place to place and the fact that it adds salts which may have some effect on the pH of poorly buffered soils. It is felt that for most studies distilled water should be used.

The use of KCl solutions as suspension media for pH determinations has not been so common in the United States as in Europe. It is recognized that soil reaction is affected by the presence of even small quantities of salts. In acid soils, the cations replace exchangeable hydrogen, and the result is a lower pH value than would be obtained with distilled water. Puri and Asghar (21) contend that, since natural soils contain varying amounts of salts, uniformity of results can only be obtained by determining soil reaction in *N* KCl solution. The pH value in *N* KCl is influenced considerably by the amount of exchangeable hydrogen and the buffer capacity of the soil. This method is not recommended for determining the pH value of soil as we commonly think of it.

SUGGESTED METHODS

From time to time the A.O.A.C. selects associate referees for method studies. In 1940 McGeorge (17) and McGeorge and Martin (18) reported on the determination of H-ion concentration of soils of arid and semiarid regions and on the pH determination of alkali soils. Purvis (22) reported on the H-ion concentration of soils of humid regions. These reports and other studies in the literature are taken into consideration in suggesting the following methods:

Determination of pH of soil at field moisture content. In order to make this determination it is necessary that the soil contain enough water to give a continuous water film between the glass and calomel electrodes.

Place an unweighed sample of soil (approximately 20-30 gm.) in a 50-ml. beaker. Add distilled water in small increments while working the sample with a stirring rod or spatula

until enough water has been added to give a visible water film on the outside of the soil mass. The soil should be soft enough to permit the ready penetration of the electrodes. (This moisture content is slightly above the moisture equivalent.)

The pH measurements may be made at once unless the soil is very dry. In this case at least 1 hour should be allowed for the water completely to penetrate the soil granules. Press the glass and calomel electrodes into the soil until the sensitive portions are completely covered by the wet soil. Make the pH reading, raise the electrodes, and again press them into the soil mass. Several readings should be made in this manner. This is necessary, since the first reading may be in error because of failure to replace the film of distilled water on the electrode by a film of water from the soil.

Determination of pH of soil suspensions. When pH is determined for purposes of chemical characterization of a soil, measurements should be made under equilibrium conditions with controlled CO₂ pressure if the results are to be reproducible. It is also desirable that the soil suspension be agitated during or just preceding the reading.

For this determination it is suggested that a 1:1 ratio of soil:water be used. Some type of bubbling tube or electrode vessel is desirable. Vessels for this purpose have been described by Gardner and Whitney (9) and Bailey (1).

Weigh a convenient amount of soil into a beaker and add an equal weight of distilled water. Stir the suspension and allow it to stand for $\frac{1}{2}$ hour or a moderately longer period. Then transfer it to a bubbling tube, and pass gas of constant CO₂ content into the suspension for several minutes. If ordinary air (0.03 per cent CO₂) is used in aspiration, the condition that results should approximate that which would be attained by mechanical stirring. Occasional samples require 20 or 30 minutes to reach equilibrium. If a single compartment tube is used, stop the flow of gas and make the pH reading immediately. If a two-compartment tube is used, the measurement may be made while the gas bubbles keep the soil particles in suspension.

Information on determination of pH under controlled CO₂ pressure is relatively meager, and further study is needed.

REFERENCES

- (1) BAILEY, E. H. 1932 The effect of air drying on the hydrogen-ion concentration of the soils of the United States and Canada. U. S. Dept. Agr. Tech. Bul. 291.
- (2) BAILEY, E. H. 1943 The importance of agitation of the soil suspension with the glass electrode. *Soil Sci.* 55: 143-146.
- (3) BAYER, L. D. 1927 Factors affecting the H-ion concentration of soils. *Soil Sci.* 23: 399-414.
- (4) CAROLUS, R. L., AND LUCAS, R. E. 1943 Some factors influencing fluctuations in acidity during periods of extreme change in the moisture content of soils. *Proc. Amer. Soc. Hort. Sci.* 42: 507-510.
- (5) CHAPMAN, H. D., OXLEY, J. H., AND CURTIS, J. H. 1940 The determination of pH at soil moisture contents approximating field conditions. *Proc. Soil Sci. Soc. Amer.* 5: 191-200.
- (6) CLARK, W. M. 1923 The Determination of Hydrogen Ions, ed. 3. Williams and Wilkins Co., Baltimore.
- (7) DAVIS, L. E. 1943 Measurements of pH with the glass electrode as affected by soil moisture. *Soil Sci.* 56: 405-422.
- (8) DOLE, M. 1941 The Glass Electrode. John Wiley & Sons, Inc., New York.
- (9) GARDNER, R., AND WHITNEY, R. S. 1943 The effect of carbon dioxide on soil reaction: II. An apparatus for the electrometric titration of soil suspensions with carbonated water. *Soil Sci.* 56: 63-65.
- (10) HAAS, A. R. C. 1941 The pH of soils at low moisture content. *Soil Sci.* 51: 17-39.
- (11) HESTER, J. B., AND SHELTON, F. A. 1933 Seasonal variations of pH, a factor in making lime recommendations. *Jour. Amer. Soc. Agron.* 25: 299-300.

- (12) HUBERTY, M. R., AND HAAS, A. R. C. 1940 The pH of soil as affected by soil moisture and other factors. *Soil Sci.* 49: 455-478.
- (13) KEATON, C. M. 1938 A theory explaining the relation of soil-water ratios to pH values. *Soil Sci.* 46: 259-265.
- (14) McGEORGE, W. T. 1935 The measurement and significance of hydroxyl-ion concentration in alkaline calcareous soils. *Ariz. Agr. Exp. Sta. Tech. Bul.* 57.
- (15) McGEORGE, W. T. 1937 The determination of soil reaction under field conditions by means of the spear-type electrode. *Jour. Amer. Soc. Agron.* 29: 841-844.
- (16) McGEORGE, W. T. 1938 Factors contributing to the reaction of soils and their pH measurement. *Ariz. Agr. Exp. Sta. Tech. Bul.* 78.
- (17) McGEORGE, W. T. 1940 Report on H-ion concentration of soils of arid and semi-arid regions. *Jour. Assoc. Off. Agr. Chem.* 23: 204.
- (18) McGEORGE, W. T., AND MARTIN, W. C. 1940 pH determination of alkali soils. *Jour. Assoc. Off. Agr. Chem.* 23: 205-219.
- (19) MASON, D. D., AND OBENSHAIN, S. S. 1938 A comparison of methods for the determination of soil reaction. *Proc. Soil Sci. Soc. Amer.* 3: 129-137.
- (20) PIERRE, W. H. 1925 The H-ion concentration of soils as affected by carbonic acid and the soil-water ratio and the nature of soil acidity as revealed by these studies. *Soil Sci.* 20: 285-305.
- (21) PURI, A. N., AND ASGHAR, A. G. 1938 Influence of salts and soil-water ratio on pH value of soils. *Soil Sci.* 46: 249-257.
- (22) PURVIS, E. R. 1940 Report on hydrogen-ion concentration of soils of humid regions. *Jour. Assoc. Off. Agr. Chem.* 23: 219-221.
- (23) SNYDER, E. F. 1935 Methods for determining the hydrogen-ion concentration of soils. U. S. Dept. Agr. Cir. 56.
- (24) WHITNEY, R. S., AND GARDNER, R. 1943 The effect of carbon dioxide on soil reaction. *Soil Sci.* 55: 127-141.
- (25) WILCOX, J. C. 1936 Some factors involved in the colorimetric determination of pH of soils. *Sci. Agr.* 16: 225-232.

SOIL CONTENT OF FLUORINE AND ITS DETERMINATION

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Fluorine has been designated as one of the "neglected soil constituents that affect plant and animal development" (27, p. 820). Clarke (5) computed a fluorine incidence of 0.02 per cent in the lithosphere and gave 0.10 per cent as the mean content for 73 specimens of igneous rocks. Steinkoenig (33) reported a fluorine content of 0.03 per cent for nine Pennsylvania soils and subsoils and attributed the occurrence of the element to the grains of "biotite, tourmaline, muscovite, apatite, fluorite, and phlogopite." Analyses of both natural and fluoride-treated soils have been reported also by the Kentucky (16) and Tennessee Stations (20).

Since fluorine occurs in such small amounts in soils, and may be absent, it has been regarded as a nonessential element that exerts no direct effect upon plant growth. Bartholomew (2, 3) studied the rôle of fluorine carried by incorporations of rock phosphate, and work conducted at the Tennessee Station demonstrated that the fertilizer value of fusions of the rock is governed by degree of defluorination (26).

A more recent aspect of the fluorine problem is that of the behavior and fate of fluorides brought to the soil through fertilizers, slags, and insecticides and, to a meager extent, by rain water. The effects that additive fluorides may exert upon germination and upon plant responses have been reported by Morse (28), by Bartholomew (2), and by other workers cited by Willis (35, pp. 358-366). A comprehensive review of the literature on fluorine was given by McClure (15). Sherman (32) concluded that additive fluorides induce the oxidation of manganese compounds in both acidic and alkaline soils. Kelly and Midgley (12) postulated that "fluoride ions" diminish "the phosphate-fixing capacity of the soil, thus causing increased availability of applied phosphates," whereas a different explanation of the effect of fluorides upon the dissolvability of phosphates has been advanced in contributions from the Tennessee Station (22, 23, 24).¹

Incorporation of barium silicofluoride at heavy rates was proposed for the extermination of larvae of the Japanese beetle in Pennsylvania and in New Jersey (8, 13, 14). This prompted a 4-year lysimeter study of the fate of such incorporations, alone and with limestone and with dolomite, and the results indicated that calcium fluoride is the ultimate combination to which additive fluorine passes in the soil (17).

When rock phosphate is acidulated, most of its fluorine content remains in the resultant superphosphate. Although the fluoride components of superphosphate were considered inert, it has been demonstrated that they bring about sub-

¹ See also Nagelschmidt, G., and Nixon, H. L. 1944 Formation of apatite from superphosphate in the soil. *Nature* 154: 428. This paper was published September 30, subsequent to submittal for publication of the present article.

stantial decreases in P_2O_5 availability when superphosphates are processed by additions of liming materials (18) and defluorinated rock phosphate calcines (4, 21). This lessened availability is registered by chemical tests and by plant response and has been attributed to reversion of tricalcium phosphate to apatite combination (18, 23, 30). It was concluded, however, that a similar diminution does not occur when superphosphate is incorporated with limed soils (23, 24). Regardless of form and carrier, calcium fluoride incorporations exerted no toxic effect upon germination and induced no significant increase in the fluorine content of either red clover or Sudan grass (25). This proved true even when the fluoride was incorporated in amount beyond that which would be introduced by 900 incorporations of superphosphate at the rate of 500 pounds per acre.

After Hart *et al.* (10, 29) had concluded that the extended use of fluoride-bearing phosphates caused no enhancement in the fluorine content of forage crops, and hence had not created a hazard in livestock feeding, they raised the question as to whether the additive fluorides would pass into ground waters and endanger the public health. This aspect will be considered in subsequent presentation of findings obtained over an extended period in extensive lysimeter studies as to the outgo of fluorine from repetitive annual additions of superphosphate and from incorporations of quenched calcium silicate slag, which carries 6 per cent of calcium fluoride.

DETERMINATION OF THE FLUORINE CONTENT OF SOILS

It has been observed that "quantitative determination of fluorine has been recognized as a difficult and tedious procedure" (9). Fahey (7) noted that 20 analytical technics—gravimetric, volumetric, colorimetric, and nephelometric—were proposed during the 120-year period between the appearance of the Berzelius method and the literature review by Stevens, and that Merwin's modification of Steiger's method is used widely in rock analysis. The lead chlorofluoride technic developed by Hoffman and Lundell (11) has proved dependable for the analysis of materials of relatively high fluorine content.

None of these methods was applicable, however, to the determination of the minute percentage of fluorine in soils, and until recently there was no prescribed procedure for this determination. The use of thorium nitrate for the titration of dilute solutions of fluorides was proposed by Willard and Winter (34) and represented a distinct contribution. After the solute fluoride is titrated to thorium fluoride, further addition of the titrant reacts with the zirconium-alizarin sulfonate indicator to form a "lake," which registers the determinative change in tint. The parallel values obtained by titration of alcoholic and aqueous aliquots containing 1–5 mgm. of fluorine and the necessity for the use of 48 per cent alcohol systems and empirical standardization of the thorium nitrate titrant were demonstrated by Hammond and MacIntire (9).

With the adaptation of the Willard and Winter procedure to the titrative determination of fluorine in solutions of meager fluorine content, considerable research still was required to assure complete distillation of the fluorine content of an appropriate analytical charge of soil. Alkali fusions and magnesic incin-

erations of the analytical charges proved inadmissible (20). Prerequisites for the distillation of entire fluorine content of soils are (a) preparatory fixation of the element and its conversion to compounds that undergo dissolution during digestion and yield the element to the distillates, (b) elimination of "volatiles" that would pass into the distillates and vitiate their titration, (c) proper temperature control, and absence of colloidal silica and the prevention of bumping during distillation. It was found that the admixed calcium peroxide assures the fixation of the full fluorine content of the soil during the preparatory step of ignition and also assures that all of the fluorine will pass from the digestate (20). Since fluorine-free peroxide of calcium is not always obtainable, defluorinated calcium hydroxide was substituted by Clifford (6). The use of the balanced current of steam prevents bumping and diminishes by half the time required for the complete expulsion of fluorine by the perchloric acid.

As the result of findings of the citations and through collaborative studies upon natural and fluoride-fortified soils, the procedure adopted is as follows:

Analytical sample

From a 2-mm.-sieved reserve sample of air-dried soil, sift the portion finer than 0.5 mm., using a rubber-tipped pestle to disintegrate lumps, and determine the proportion sifted. Mix thoroughly the 0.5-mm.-sifted material and grind a 10-gm. portion to pass a 325-mesh sieve, and preserve in a stoppered container.

Distillation apparatus

Pyrex glassware should be used for the pictured unit (1, p. 15), as adapted in multiple for passage of steam (19) and modified by substitution of the Classen flask in lieu of the Kjeldahl, or for either of the multiple-unit equipments (25, 31). The reaction flask should be scoured with quartz sand after every usage to remove any accumulations of silica.

Comparison tubes

The aliquot titrations should be made in colorless white elongated Nessler tubes, and the aliquots should be stirred during titration by means of a long glass rod, one end of which is bent into a circle with diameter at right angles to the straight section.

Reagents

Distilled water as obtained by the redistillation of ordinary distilled water containing a few drops of H_2SO_4 and colored with KMnO_4 , the initial fraction of distillate being discarded.

Fixative agencies. Either fluoride-free CaO_2 or a defluorinated Ca(OH)_2 . To obtain the hydroxide, slake 56 gm. of marble-derived lime and dissolve in 250 ml. of 60 per cent perchloric acid, added slowly with stirring; boil the resultant solution to fumes; dilute with 300 ml. of distilled water and again boil to fumes, and repeat this operation twice; dilute and filter to remove SiO_2 . Pour the filtrate into 1 liter of a 10 per cent solution of c.p. NaOH ; allow the precipitate to settle, and wash by centrifugation (6, p. 360). The resultant fluoride-free Ca(OH)_2 should be dried in CO_2 -free air and kept protected against CO_2 .

Perchloric acid. Concentration of 60 per cent.

Silver sulfate. The c.p. solid.

Phenolphthalein solution. Concentration of 0.1 per cent in 1 + 1 alcohol.

Sodium alizarin sulfonate indicator. Concentration of 0.05 per cent in aqueous solution.

Thorium nitrate titrant. Normality of 0.01, standardized against c.p. sodium fluoride, in 1 + 1 alcoholic solution adjusted to $\text{pH } 3 \pm 0.2$, with 2.0 ml. of 0.05 *N* HCl .

Determination

For soils of relatively high fluorine content, use a 0.5-gm. charge of the 325-mesh sample; for those of low content, use a 1-gm. charge. Mix the charge intimately with either the peroxide or the hydroxide of calcium in a nickel or a platinum crucible. Incinerate thoroughly in an electric furnace below 500° C., and then ignite 30 minutes at 900° C. Cool and transfer the ignited mixture into the Classen flask, the interior of which should be devoid of silica coating. Wash down the walls of the flask by dropwise addition of 5 ml. of distilled water. Introduce a spatula-tip portion of silver sulfate. Add 3 drops of the phenolphthalein solution; neutralize with perchloric acid and add 15 ml. additional. Connect the Classen flask with a condensor. Use a small flame to bring the solution-suspension to 125° C.; inject a current of steam and bring the system to 135° ± 5° C. Maintain this temperature during the steam distillation to a collection of 200–250 ml. distillate in a calibrated 250-ml. flask and make to volume.

Dilute a 25-ml. aliquot with an equal volume of alcohol; introduce 10 drops of the sodium alizarin sulfonate; neutralize with 0.05 N NaOH and then adjust pH to 3.0 with 2.5 ml. of 0.05 N HCl. Titrate with the empirically standardized 0.01 N thorium nitrate to the same pink end point of the correspondingly treated blank. Express results as parts per million or as percentage of soil.

REFERENCES

- (1) Association Official Agricultural Chemists 1940 Official and Tentative Methods of Analysis, ed. 5. Washington, D. C.
- (2) BARTHOLOMEW, R. P. 1935 Fluorine, its effect on plant growth and its relation to the availability of phosphorus in phosphate rocks. *Soil Sci.* 40: 203–217.
- (3) BARTHOLOMEW, R. P. 1937 Availability of phosphate rocks in soils of varying degree of acidity. *Jour. Amer. Soc. Agron.* 29: 293–298.
- (4) BEESON, K. C., AND JACOB, K. D. 1938 Chemical reactions in fertilizer mixtures—reactions of calcined phosphate with ammonium sulfate and superphosphate. *Indus. and Engin. Chem.* 30: 304–308.
- (5) CLARKE, F. W. 1908 The data of geochemistry. *U. S. Geol. Survey Bul.* 330: 31; 1916 *Bul.* 616: 27, 32, 34; 1924 *Bul.* 770: 34.
- (6) CLIFFORD, P. A. 1941 Report on fluorine. *Jpur. Assoc. Off. Agr. Chem.* 24: 360–361.
- (7) FAHEY, J. J. 1939 Colorimetric determination of fluorine with ferron. *Indus. and Engin. Chem., Analyt. Ed.* 11: 362–363.
- (8) GUYTON, T. L. 1929 The Japanese beetle in Pennsylvania. *Penn. Dept. Agr. Bul.* 473.
- (9) HAMMOND, J. W., AND MACINTIRE, W. H. 1940 Thorium nitrate titration of micro quantities of fluorine in aqueous and alcoholic systems. *Jour. Assoc. Off. Agr. Chem.* 23: 398–404.
- (10) HART, E. B., PHILLIPS, P. H., AND BOHSTEDT, G. 1934 Relation of soil fertilization with superphosphates and rock phosphate to fluorine content of plants and drainage waters. *Amer. Jour. Pub. Health* 24: 936–940.
- (11) HOFFMAN, J. I., AND LUNDELL, G. E. F. 1929 Determination of fluorine and of silica in glasses and enamels containing fluorine. *U. S. Dept. Com. Bur. Standards Res. Paper* 110.
- (12) KELLY, J. B., AND MIDGLEY, A. R. 1943 Phosphate fixation—an exchange of phosphate and hydroxyl ions. *Soil Sci.* 55: 167–176.
- (13) LEACH, B. R., AND LIPP, J. W. 1926 A method of grub-proofing turf. *U. S. Golf Assoc., Green Sect. Bul.* 6.
- (14) LIPP, J. W. 1929 Studies of substitutes for arsenate of lead as a soil insecticide. *Jour. Econ. Ent.* 22: 600.
- (15) McCLEURE, F. J. 1933 A review of chlorine and its physiological effects. *Physiol. Rev.* 13: 277–300.

- (16) MCHARGUE, J. S., AND HODGKISS, W. S. 1939 Report on less common elements in soils. *Jour. Assoc. Off. Agr. Chem.* 22: 249-252.
- (17) MACINTIRE, W. H., SHAW, W. M., AND ROBINSON, B. 1935 The fate of added BaSiF_6 and its effect upon sulfates and other soil components. Univ. Tenn. Agr. Exp. Sta. Bul. 155.
- (18) MACINTIRE, W. H., ET AL. 1937 Development of P_2O_5 insolubility in phosphatic mixtures—the formation of fluorapatite as its cause. *Indus. Engin. Chem.* 29: 758-766.
- (19) MACINTIRE, W. H., SHAW, W. M., AND HARDIN, L. J. 1938 Direct determination of the available P_2O_5 content of fertilizers. *Indus. Engin. Chem., Analyt. Ed.* 10: 144-152.
- (20) MACINTIRE, W. H., AND HAMMOND, J. W. 1939 Use of peroxides of calcium and magnesium in determination of fluorine content of soils, siliceous materials, and organics. *Jour. Assoc. Off. Agr. Chem.* 22: 231-236.
- (21) MACINTIRE, W. H., AND HARDIN, L. J. 1940 Fluoride-induced reversion in mixtures of superphosphates and calcined rock phosphate. *Indus. and Engin. Chem.* 32: 88-94.
- (22) MACINTIRE, W. H. 1941 A new explanation of what happens to superphosphate in limed soils. Univ. Tenn. Agr. Exp. Sta. Bul. 176.
- (23) MACINTIRE, W. H., AND HATCHER, B. W. 1942 Evidence in support of a new concept as to the end product of superphosphate in limed soils. *Soil Sci.* 53: 43-54.
- (24) MACINTIRE, W. H., AND HATCHER, B. W. 1942 The beneficial effects of preliming upon PO_4 -uptake from incorporations of water-soluble calcium phosphate. *Jour. Amer. Soc. Agron.* 34: 1010-1015.
- (25) MACINTIRE, W. H., ET AL. 1942 The fluorine content of certain plants fertilized with phosphates and slags carrying fluorides. *Indus. and Engin. Chem.* 34: 1469-1479.
- (26) MACINTIRE, W. H., ET AL. 1944 Fused tricalcium phosphate: relation of degree of defluorination to fertilizer value of quenched fusions of rock phosphate. *Soil Sci.* 57: 425-442.
- (27) MCMURTREY, J. F., JR., AND ROBINSON, W. O. 1938 Neglected soil constituents that affect plant and animal development. In *Soils and Men*. U. S. Dept. Agr. Yearbook.
- (28) MORSE, H. H. 1935 The toxic influence of fluorine in phosphatic fertilizers on the germination of corn. *Soil Sci.* 39: 177-195.
- (29) PHILLIPS, R. H., HART, E. B., AND BOHSTEDT, G. 1934 Does fluorine in phosphorus fertilizers endanger the public health? Wis. Agr. Exp. Sta. Bul. 430.
- (30) RADER, L. F., JR., AND ROSS, W. H. 1939 Effect of fluorine in the determination of citrate-insoluble phosphoric acid by the official method. *Jour. Assoc. Off. Agr. Chem.* 22: 400-408.
- (31) REYNOLDS, D. S., KERSHAW, J. B., AND JACOB, K. D. 1936 Multiple-unit distilling apparatus for determination of fluorine by the Willard and Winter method. *Jour. Assoc. Off. Agr. Chem.* 19: 156-162.
- (32) SHERMAN, G. D., MCHARGUE, J. S., AND HAGEMAN, R. H. 1943 The influence of halides on the oxidation of manganese in soil. *Soil Sci.* 56: 127-134.
- (33) STEINKOENIG, L. A. 1919 Relation of fluorine in soils, plants, and animals. *Indus. and Engin. Chem.* 11: 463-465.
- (34) WILLARD, H. H., AND WINTER, O. B. 1933 Volumetric method for determination of fluorine. *Indus. and Engin. Chem.* 5: 7-10.
- (35) WILLIS, L. G. 1939 Bibliography—The Minor Elements, ed. 3. Chilean Nitrate Educational Bureau, Inc., New York.



Charles Bernard Lipman

Charles Bernard Lipman

1883-1944

Charles Bernard Lipman, a consulting editor of *SOIL SCIENCE* since its foundation in 1916 and senior author of the initial scientific paper published in this *Journal*, died in Berkeley, California, October 22, 1944.

Born in Moscow, Russia, August 17, 1883, he emigrated to the United States with his family in 1888.

In 1904 he received the bachelor of science degree from Rutgers University, which 30 years later awarded him the honorary degree of doctor of science in recognition of his outstanding achievements.

Having obtained the master of science degree from the University of Wisconsin in 1909, he was called to the University of California, where he was to spend his entire professional life. His appointment and his career there are described briefly by his colleague Professor John S. Burd:

In the early part of the present century, the late Professor E. W. Hilgard, dean of the College of Agriculture of the University of California, became deeply interested in the newer developments of soil microbiology, a field with which he, himself, had had little to do, and in which the university had no one actively engaged. As a result, it was decided to engage some young man of promise in the hope that he might make valuable discoveries and contributions to our knowledge of the microbiology of the semiarid and arid soils characteristic of this region.

Charles B. Lipman was selected for this responsibility and soon became recognized both for his studies in his field of interest and for his usefulness to the university in academic and administrative positions. He pursued his studies for the doctorate and obtained that degree in 1910 under the advice and counsel of Professor Hilgard, the late Jacques Loeb, and W. J. V. Osterhout.

His contributions to microbiology, plant nutrition, and to soil science in general are a matter of record. As dean of the Graduate Division he assumed a leading place among American educators and was accorded the respect and esteem of all who knew him in this relation. His ability to secure the confidence of men of large affairs and great responsibility was a potent source of his success in forwarding and sustaining research and scholarship in America.

Dr. Lipman had a flair for social life, and he used his limited vacations, for the most part, in association with congenial friends at the many clubs to which he belonged, and particularly at the summer encampments of the Bohemian Club, where all were welcome and assured of hospitable entertainment at his private camp.

The esteem in which Dr. Lipman was held as scientist, educator, and man is expressed thus by another of his colleagues, Dr. W. P. Kelley:

Endowed, as he was, with a vivid imagination and pronounced curiosity about the living world, Charles Lipman devoted much of his energy to the exploration of new fields. Early in his scientific career, he became interested in the then little known microbiology of arid and semiarid soils, a subject on different phases of which he published several papers. A little later his attention was drawn to the relatively new field of the minor elements. He made noteworthy contributions to the role of copper, zinc, and boron in the growth and development of higher plants and of microorganisms. Still later, Dr. Lipman

made a number of studies on certain coral atolls in the Caribbean and in the Pacific, investigating soil formation, the deposition of calcium carbonate, and the microflora. Later still, he became acutely interested in the question of the longevity of life and the effects of extreme desiccation and low temperature on the viability of organisms. In all these fields, Dr. Lipman's work was largely of a pioneering character, and in all of them he demonstrated originality and boldness of attack.

The many manifestations of physiological disorder in the economic plants of California attracted Dr. Lipman's attention. He devoted considerable study to the chlorosis and dieback of fruit trees and the mottle leaf of citrus. It is but natural, as an outgrowth of these investigations, that he should have taken special interest in the general physiology of plants. In the later period of Dr. Lipman's work, his attention was focused increasingly on plant physiology rather than on the soil.

Charles Lipman was a stimulating teacher. His lectures were lucid and well presented. The advanced seminars which he conducted were particularly effective. He had a well-developed faculty of analyzing published literature. Always he strove to develop the critical attitude in his students and to emphasize basic principles. He held that the thorough training of students in the basic sciences, literature, and the humanities was the best preparation for life whether on the farm, in the laboratory, or in the office.

Throughout his adult life, Dr. Lipman was characterized by pronounced idealism. This took various forms. It was shown in his attitude toward the organization and work of the Agricultural Experiment Station. On several occasions he vigorously upheld the view that progress in the art of crop production and animal husbandry can best be promoted through the elucidation and understanding of the basic principles on which crop growth and animal life rest. For this reason a substantial part of the activities of the Experiment Station should, he contended, be devoted to the investigation of fundamental principles rather than to empirical experimentation or the perfection of the art of agriculture.

His idealism enabled him to exert a potent influence on the Graduate Division of the University of California, of which he was dean for the last 21 years of his life. During this period standards were raised, and largely through his influence the requirements for advanced degrees were broadened and liberalized in several departments of the university. He consistently stood for scholarly attainment in contrast to mere technical proficiency. His work as dean enabled him to become acquainted with graduate work throughout the university and with the instruction given in the various undergraduate curricula of universities and colleges throughout America, as well as in many foreign countries. The office of dean brought Dr. Lipman into close contact with the leading educators of the nation.

Charles Lipman grew with the years. He had a strongly developed sense of the fitness of things, and especially was he a champion of right living. He had no patience with shady dealings or shoddy thinking. His principles were compelling. He could never countenance the taking of an unfair advantage. Although aristocratic in the best sense of the word, Dr. Lipman was a genuine democrat and he often expressed warm sympathy for the unfortunate. He felt strongly that in an industrial civilization, it becomes increasingly necessary for organized society to show effective concern for the underprivileged, that in a real sense the underprivileged is a victim of circumstances over which he has no control. He clearly recognized the interdependence of the several strata of society. He had a highly developed spiritual sense and often championed moral principles consistent with the highest Christian ethics. His idealism found its highest expression in the humanitarian and moral spheres.

The cloistered atmosphere of the university did not prevent Charles Lipman from exercising his rights and duties of citizenship. He took a lively interest in public affairs, national and international, and followed current political events closely. He often discussed with his friends the slipshod, unintelligent, and sometimes fraudulent statements of politicians and publicists. He could not tolerate bigotry in any form or quarter. He believed strongly in international cooperation in the maintenance of peace, and was op-

posed to isolationism on the part of America, whether in the political, economic, or any other field.

As the years passed and opportunity was afforded for intimate acquaintance with Charles Lipman, the writer was often reminded of the similarities between him and his beloved brother, the late Jacob G. Lipman. They had many traits in common and were actuated by the same philosophy of life. They held much the same ideals and alike were able to present their views convincingly. Both had a pronounced sense of humor and were gifted in the art of conversation, enlivening their discourse with humorous tales and anecdotes, of which they each possessed an inexhaustible store.

FACTORS IN PERMEABILITY CHANGES OF SOILS AND INERT GRANULAR MATERIAL

ARTHUR F. PILLSBURY AND DAVID APPLEMAN

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Trapped air has frequently been found to influence the movement of water through soil (1, 5, 9, 10). Considerable recent research has been concerned with the effect of such trapped air upon permeability and with the persistence with which that air is held in the soil. The data reported in this paper show that (a) some air is removed from soil only when water is continuously applied until the air is dissolved, and (b) such trapped air effectively decreases permeability.

The work of Smith and Browning (11) relates "persistent water-unsaturation" to percolation rates and other soil factors. Extensive studies are being made by the Regional Salinity Laboratory of the Bureau of Plant Industry, U. S. Department of Agriculture, in connection with the infiltration capacity and factors influencing permeability of water-spreading basins.²

Since the hydraulic slope was measured in the work herein reported, permeability is in all cases referred to as the coefficient of permeability (K_s). K_s = apparent velocity \div hydraulic slope. The unit used is centimeters per hour.

In the fall of 1942 laboratory permeability measurements, using distilled water, were made on a number of soils. Percolation rates for Placentia loam, surface foot, were typical, and are shown in figure 1. An initial period of decreasing permeability is followed by a period of increasing permeability and, in turn, by a final period of decline. Bodman (2) and Fireman and Bodman (4) show some permeability curves of similar shape. The data of curve A were first obtained, starting with a dry soil and wetting from the top downward. On the supposition that the bulk of any trapped air would be displaced if the soil was gradually wet from the bottom, that procedure was next followed. When water had risen until it stood 1 inch over the top of the soil in the cylinders, it was allowed to stand for 24 hours. The run was then started with flow downward. The results for the comparable Placentia loam (fig. 1, curve B)

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² A copy of J. E. Christiansen's manuscript, "Effect of Entrapped Air Upon the Permeability of Soils" (subsequently published in *Soil Sci.* 58: 355-365, 1944) reached us after the present manuscript was submitted for publication. There has been some duplication of effort, but the work of the two laboratories was carried on independently, and the results of both endeavors appear to have been made richer thereby. Impetus for the work resulted from an appeal by H. L. Haehl, consulting engineer of San Francisco, who was faced with the practical necessity of improving the permeability characteristics of water-spreading basins in the San Joaquin Valley. We gratefully acknowledge the courtesy of O. C. Magistad and J. E. Christiansen, of the Regional Salinity Laboratory, in referring Mr. Haehl to us. We desire to thank our associate M. R. Huberty and also Mr. Christiansen and Milton Fireman, of the Regional Salinity Laboratory, for their helpful suggestions in reviewing the manuscript.

indicate that somewhat more air may have been displaced, but the same character of curve persisted.

At the same time, in connection with sorption curve work (6), it was observed that the computed pore space of some soil cores was not completely filled when wet from the bottom.

In the fall of 1943 a permeameter was set up in a 20°C. constant temperature room. The soil was placed in vertical glass cylinders of 3.2 cm. diameter with glass wool plugs at the bottom. The length of the column of soil was 16 cm., and the cylinders were equipped with manometers to measure the hydraulic slope in the central 10-cm. parts of the columns. The overall head, from a constant level reservoir to the outlets under the cylinders, was approximately 40 cm. The cylinders discharged into burettes. Rates of flow, frequently

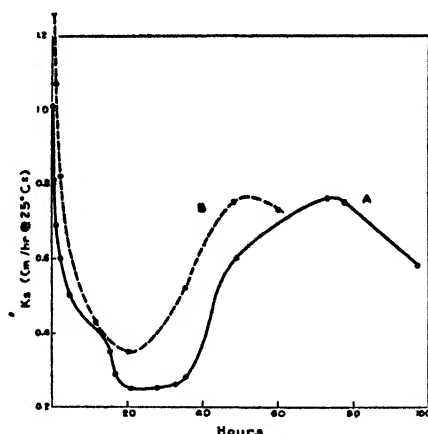


FIG. 1. ORIGINAL PERMEABILITY MEASUREMENTS OF PLACENTIA LOAM, SURFACE FOOT

A, initially dry soil; B, same soil wet from bottom until water stood 1 inch over top, where it was allowed to remain for 24 hours before runs were started. Each curve is an average of 6 runs.

determined from timing the filling of the burettes, were checked periodically by measuring the total leachate collected below.

At the time the apparatus was constructed it was suggested that CO_2 might be a factor in permeability. Provision was therefore made to keep the entire air system from the reservoir to the flasks of leachate free of CO_2 . Preliminary runs indicated, however, that these precautions had no measurable effect on the permeability, and CO_2 was not excluded after run 36. Distilled water was used. Unless otherwise specified, it was first boiled and then stored in such a way as to keep it free of air and CO_2 while cooling and prior to use. Equal weights of dry soil were placed loosely in each cylinder, and the cylinders were then lightly tapped until measurable settlement ceased.

Our original numbering of the "runs" has been retained, i.e., nos. 11 to 16 were the first simultaneous set, 21 to 26 were the second, etc. The only runs excluded herein (except as otherwise noted) were of a rough preliminary nature or were runs in which the manometers failed to function properly.

Permeabilities for runs 11 to 16 inclusive are plotted in figure 2 against the milliliters of leachate per gram of soil. For the work with this one soil it was found that rate changes were better synchronized with time than with the amount of leachate. Time is therefore plotted against K_s in all other charts. Figures 3 and 4 both show the average curve for runs 11 to 16 with K_s plotted against time.

Periodic analyses were made of the leachate from each run. The data indicate a continuous leaching of decreasing magnitude, as illustrated in figure 3. After the first 20 hours or so the concentrations have no significant correlation with rate. The wetting could be expected to weaken colloidal aggregates, and, with movement of water through the soil, such loosened particles could be expected

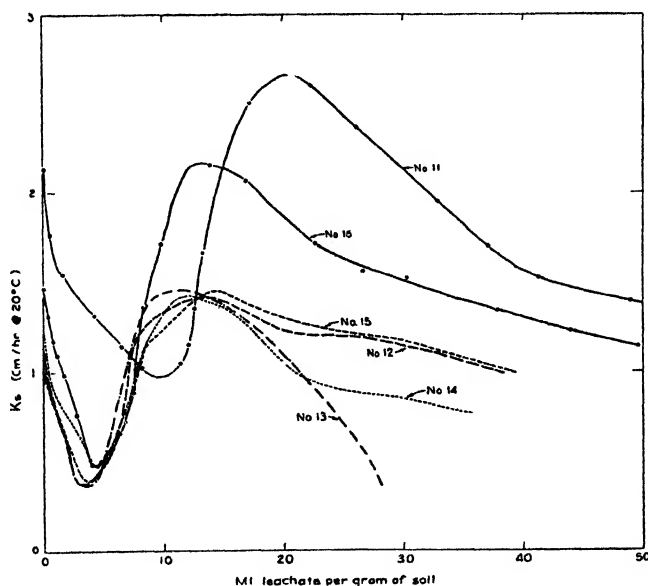


FIG. 2. COEFFICIENTS OF PERMEABILITY FOR SIX INDIVIDUAL RUNS, ON PLACENTIA LOAM, SURFACE FOOT, PLOTTED AGAINST MILLILITERS LEACHATE PER GRAM OF SOIL (DRY BASIS)

to shift and decrease the continuity of pores, thus diminishing permeability. Removal of electrolytes could only accentuate this process by further disintegrating the aggregates. The possible effect of the growth of soil flora, which might also result in pore clogging, has not been investigated.³

The next phase of the work was to apply suction at the bottom of the cylinders, thus removing a greater portion of the air, before wetting the soil. A fluctuating suction was applied, gradually built up to 72 cm. Hg, and held there for 15 minutes. Next, the soil was wet from the top, and then the suction was released. This process compacted the soil considerably, and permeability did not approach

³ J. E. Christiansen suggests that the final period of diminishing permeability may be related to the growth of soil flora. In our tests, using distilled water, some leaching was still taking place at this time, which might also account for the decreasing rate.

the values found for previous runs. The average for six runs (nos. 21 to 26) is shown in figure 4. These data demonstrate that removal of the bulk of the air eliminated any period of increasing permeability after water was applied.

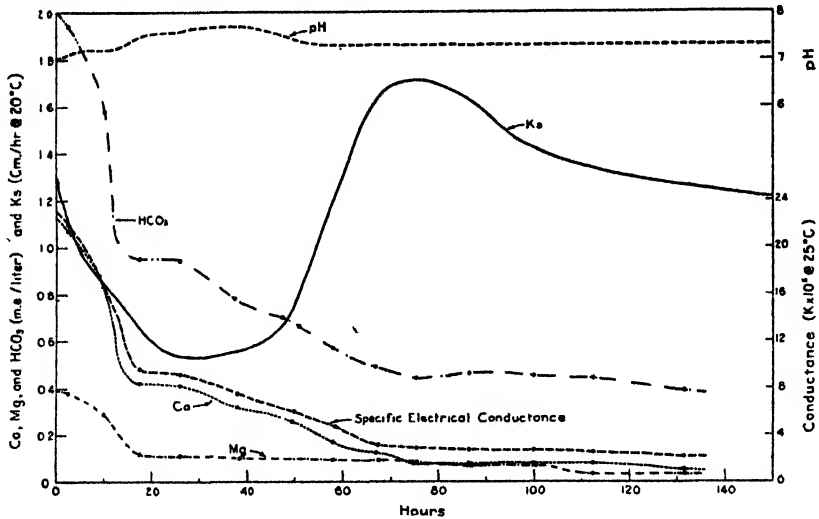


FIG. 3. COEFFICIENTS OF PERMEABILITY, pH OF LEACHATE, AND CONCENTRATION OF SEVERAL IONS IN LEACHATE, AVERAGED FOR RUNS 11 TO 16, INCLUSIVE ON PLACENTIA LOAM, SURFACE FOOT

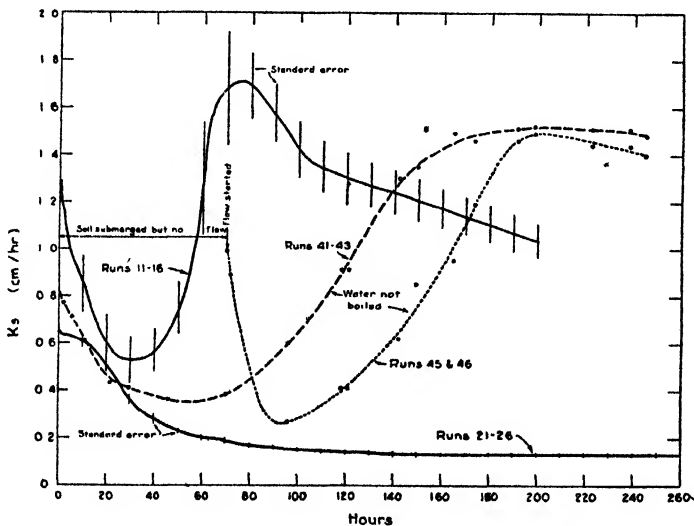


FIG. 4. COEFFICIENTS OF PERMEABILITY PLOTTED AGAINST TIME FOR RUNS, 11-16, 21-26, 41-43, AND 45 AND 46 ON PLACENTIA LOAM, SURFACE FOOT

Distilled water from the usual source has a relatively high air content, which heretofore was removed by boiling. The next test was to see how unboiled water would affect permeability. The results are shown in figure 4, runs 41

to 46 inclusive. Runs 41 to 43 were comparable with 11 to 16, except for the dissolved air in the water. The curves are similar, but there is considerable lag where the water had not been freed of dissolved air. For runs 45 and 46, the soil was submerged in water for 3 days before percolation was started, and

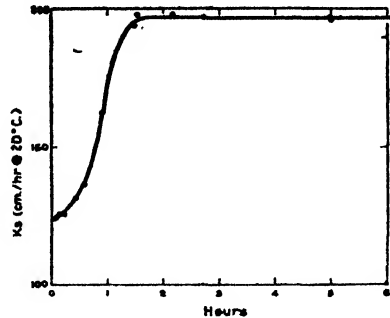


FIG. 5. TYPICAL RUN (No. 72) WITH PURE SILICA SAND (LOT A)

TABLE 1

Coefficients of permeability for various graded and ungraded samples of cleaned silica sand with boiled distilled water

RUN NO.	PARTICLE SIZE GRADATION	LOT	INITIAL K_s^*	FINAL UNIFORM K_s	PERCENTAGE, INITIAL TO FINAL K_s
	mm.		cm./hr.	cm./hr.	
104	0.589 to 0.295	A	441	468	94
105	0.295 to 0.147	A	133	140	95
101	0.295 to 0.147	B	81	128	59
121	0.295 to 0.147	B	89	115	77
122	0.295 to 0.147	B	83	106	78
102	0.147 to 0.074	B	17	35	49
123	0.147 to 0.074	B	19	34	56
124	0.147 to 0.074	B	20	35	57
103	0.074	B	0.21	0.26	81
133†	0.074	B	0.32†	0.33	97†
65	Not graded‡	A	148	182	81
72	Not graded‡	A	123	197	62

* Estimated by extrapolating curves back to zero time.

† This run was made with re-used material which had apparently become somewhat aggregated, since initial K_s was 0.34 and was followed by a drop to 0.32. Minimum rather than initial K_s is therefore used in the table. Runs with this material have been somewhat unsatisfactory because of difficulty in making the manometers function. This is one of a number of runs made with the re-used fine material—none of which have exhibited any increase in K_s greater than that shown. Although the material is not strictly inert, its use supplied evidence that no great amount of air is entrapped in the smaller pores.

‡ Predominantly 0.6 to 0.2 mm. material, but some fines.

reached maximum K_s about 2 days after runs 41 to 43. It did so, however, with about 80 per cent as much leachate.

The simplest way to eliminate any effects of soil instability and the growth of soil flora is by working with an inert soil material and distilled water rather

than with Placentia loam used heretofore. Therefore, some Corona silica sand was thoroughly and repeatedly washed in HCl, and then repeatedly rinsed to remove all impurities. After drying, a portion was ground slightly finer in a mortar to obtain a wider range of particle sizes, and then the whole was mixed. This is designated lot A. Figure 5 shows the results of a typical run, wherein there is no period of decreasing K_s , and K_s becomes constant once the air is dissolved.

The next objective was to obtain some preliminary information on the effect of particle size and particle size distribution on the entrapment of air. More silica sand was needed, and this time the sand was first ground in a ball mill, cleaned with HCl, rinsed, and then dried and sieved. This material is designated lot B. The remainder of lot A was sieved into size separates. Microscopic inspection of the particles indicated lot A to be somewhat more angular and less pitted or chipped than lot B. The surfaces of lot B particles appeared to be somewhat cleaner than those of lot A. The runs with these graded materials, and two of the ungraded lot A runs, are shown in table 1.

In a high percentage of runs reported herein, part of the soil, as indicated by a negative reading on the lower manometer, was actually under tension. The fact that tension existed affected in no measurable way the dissolving of the trapped air.

DISCUSSION

It is shown herein that when soil material is wet, air is trapped. Some air is removed by displacement—more if the soil is wet from the bottom than from the top—but sufficient remains to affect markedly the permeability characteristics of the medium. Smith and Browning (11) apparently established volumes of such trapped air by comparing pore space filled with water on wetting to pore space computed from determinations of the apparent specific gravity and the real density.

This nondisplaceable trapped air is removed only by being dissolved into the percolating waters (excluding removal by evacuation). The air content of the water entering the soil has a marked effect on the rate at which the trapped air is dissolved. As evidenced by the comparison of runs 45 and 46 with 41 to 43, and by comparison of individual run variations in other series, it appears that the water (with a given capacity to dissolve air) required to remove the trapped air from a unit volume of a given soil is not a fixed amount but is subject to variation. Part of the variation could be from differences in the amount of trapped air from sample to sample. The time the water is in contact with the air is important. Also, any tendency for the water to move through one part of the soil more rapidly than through another may affect differences. But, from a practical standpoint, the most important factors in the removal of trapped air must be the amount of water per unit volume of such air, and the capacity of the water to dissolve air. Since the solubility of air in water increases with decrease in temperature, cold waters should be more effective than warm waters.

Smith and Browning (11) suggest in their discussion, "...it appears likely that the maximum trapping of air would ordinarily occur in the intermediate range of pore sizes." The fact that an intermediate particle size (runs 102, 123, and 124) in our runs with silica sand size-separates gave the most evidence of trapped air supports this line of reasoning. More work should be done with size-separates of inert materials before very specific conclusions are drawn on the effect of pore size on entrapment of air. The apparent differences, shown in runs 105 and 101, with only slight differences in material of the same size, is a case in point.

So far as we know, there is no evidence that in actual irrigation practice, or under natural or simulated rainfall, any appreciable amounts of nondisplaceable trapped air are ever removed. It is with ground-water flows and with water-spreading basins in rather continuous use that the removal by solution is of greatest importance. With irrigation investigations and with studies of rainfall-runoff relations, it is common to conclude that infiltration capacity decreases

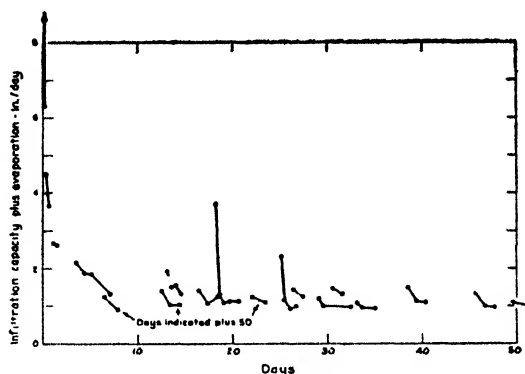


FIG. 6. INFILTRATION CAPACITY RATES FOR FIELD PLOT 1 c, INDIO VERY FINE SANDY LOAM, COACHELLA VALLEY, 1938-39

with time at a diminishing rate until it is virtually constant. In connection with results from some field basins used for studying infiltration capacities, Edlefsen (3) says: "When water is first applied to a field-plot, the rate of infiltration is comparatively rapid and gradually decreases with time to an asymptotic or approximately steady value which seems to be more or less characteristic of the plot at that particular time."

It is evident from the data of figure 6 that the entrapped air is not readily and effectively dissolved under usual field conditions. This chart shows the infiltration capacity characteristics of a plot on Indio very fine sandy loam in Coachella Valley. From December 9, 1938 to March 1, 1939, 6.3 feet of water was applied to a plot 20 by 20 feet in 19 irrigations. This plot was surrounded by an area similarly flooded. When water was applied at each irrigation, infiltration rates were at first somewhat high. This was to be expected, since there was a lag of an hour to several days between the disappearance of surface water and application of the next irrigation. These curves reflect asymptotic

rates and only a few minor indications of increasing permeability that would be caused by the dissolving of appreciable amounts of air. If water had been continuously applied, it appears probable that rates would have significantly reflected the dissolving of trapped air.

It is not inferred, of course, that the physical condition of the soil, which may affect the amount of air trapped, or the capacity of percolating waters to dissolve air, is unimportant in irrigation. To illustrate, in the course of field investigations of consumptive use (7, 8) note has been made frequently of a depression of field capacity in summer, and apparent fluctuations of field capacity with cultural operations and plant growth.

It is sometimes assumed that permeability is decreased merely by the soil's being wet for a period of time and, in consequence, undergoing physical changes such as colloidal swelling. Comparison of runs 45 and 46 with 41 to 43 does not indicate this to be the case with Placentia loam, since the initial K_s of nos. 45 to 46 was higher than that for nos. 41 to 43 despite the 3-day prior wetting. The relative steepness of the curve of nos. 45 and 46, however, indicates that, because of the prior wetting, the aggregates were less stable, once percolation started. The idea that the initial diminishing permeability is associated with an instability of the soil (which overshadows the dissolving of air) is confirmed by the failure of inert sand to show such a permeability characteristic.

CONCLUSIONS

When water starts percolating through a previously unsaturated soil, air is trapped which cannot be displaced by that water.

The maximum effect of trapped air appears to be in pores of intermediate size.

This trapped air is removed only by solution in the water percolating through the soil. The ease with which the air is dissolved depends on the capacity of the water to absorb air and on the time of contact of that water with the air, and, more important, with the amount of percolating water passing through per unit amount of trapped air.

Percolating waters pass through or around such trapped air, but the coefficient of permeability is greatly depressed thereby, increasing as air is dissolved.

In the field, it appears that such air would not be dissolved appreciably by normal rainfall or irrigation, thus allowing air-free infiltration. Exceptions would be water-spreading basins where water completely covers the surface for considerable periods and below the surface of ground-water tables.

Initial decreases in permeability are associated with the instability of soil under the action of the percolating waters. With Placentia loam topsoil, prior wetness without percolation did not decrease initial permeability but did cause permeability to drop more rapidly.

REFERENCES

- (1) BAYER, L. D. 1937 Soil characteristics influencing the movement and balance of soil moisture. *Soil Sci. Soc. Amer. Proc.* 1: 431-437.

- (2) BODMAN, G. B. 1937 The variability of the permeability "constant" at low hydraulic gradients during saturated water flow in soils. *Soil Sci. Soc. Amer. Proc.* 2: 45-53.
- (3) EDLEFSEN, N. E. 1941 A discussion. *Trans. Amer. Geophys. Union* 1941: 695.
- (4) FIREMAN, M., AND BODMAN, G. B. 1939 The effect of saline irrigation water upon the permeability and base status of soils. *Soil Sci. Soc. Amer. Proc.* 4: 71-77.
- (5) FREE, G. R., AND PALMER, V. J. 1940 Interrelationship of infiltration, air movement, and pore size in graded silica sand. *Soil Sci. Soc. Amer. Proc.* 5: 390-398.
- (6) HUBERTY, M. R. AND PILLSBURY, A. F. 1943 Solid, liquid, gaseous phase relationships of soils on which avocado trees have declined. *Amer. Soc. Hort. Sci. Proc.* 42: 39-45.
- (7) PILLSBURY, A. F. 1941 Observations on use of irrigation water in Coachella Valley, California. *Calif. Agr. Exp. Sta. Bul.* 649.
- (8) PILLSBURY, A. F., COMPTON, O. C., AND PICKER, W. E. 1944 Irrigation-water requirements of citrus in the south coastal basin of California. *Calif. Agr. Exp. Sta. Bul.* 686.
- (9) POWERS, W. L. 1934 Soil-water movement as affected by confined air. *Jour. Agr. Res.* 49: 1125-1133.
- (10) SLATER, C. S., AND BYERS, H. G. 1931 A laboratory study of the field percolation rates of soils. *U. S. Dept. Agr. Tech. Bul.* 232.
- (11) SMITH, R. M., AND BROWNING, D. R. 1942 Persistent water-unsaturation of natural soil in relation to various soil and plant factors. *Soil Sci. Soc. Amer. Proc.* 7: 114-119.

TOTAL ORGANIC SULFUR AND HUMUS SULFUR OF MINNESOTA SOILS¹

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Although much attention has been devoted to soil organic matter, the amount and form of sulfur which it contains has received scant consideration. The organic phosphorous, on the other hand, has been the subject of numerous investigations. Investigations concerning sulfur have been confined almost exclusively to the total and the readily soluble sulfate sulfur of the soil and to sulfur in the atmosphere which is a source of sulfur for the soil.

Within Minnesota, sizable areas of chernozem, black prairie, and podzol soils are found; and within the podzol region many fields have been found on which sulfur carriers cause marked increases in the growth of the crops that have the greatest demand for this nutrient (1). With the existence of adjacent areas of these great soil groups and the occurrence of a sulfur deficiency in one, the state is well suited to a study of the content and distribution of sulfur in the soil (fig. 1).

REVIEW OF THE LITERATURE

Alway, Marsh, and Methley (2) have pointed out that the whole problem of sulfur supply has received little attention as compared with investigations concerning other plant nutrients. Most of the earlier workers on sulfur have presented data on the total amount of sulfur in the soil. In any total analysis little information is gleaned regarding the availability of any specific plant nutrient. The more recent investigations on the sulfur problem have included information pertaining to the available or water-soluble sulfates and to the atmospheric sulfur supply.

Studies on sulfate sulfur have been reported by Brown and Kellogg (5) for Iowa soils, by Ames and Boltz (3) for Ohio soils, and by McAuliffe³ for Minnesota soils. Other investigations of this nature have been conducted at various agricultural experiment stations. Studies on the atmospheric sulfur in Minnesota have been made by Alway, Marsh, and Methley (2). The results of all these investigations are in agreement in that they have demonstrated that the amounts of sulfate sulfur and atmospheric sulfur are extremely variable. They have also shown that sulfate sulfur other than that in the form of barium sulfate is rapidly leached from the soil.

¹ Herman Frasch Foundation for Research in Agricultural Chemistry, Paper No. 226. Paper No. 2186, Scientific Journal Series, Minnesota Agricultural Experiment Station.

² Research fellow and professor of soils, respectively.

³ McAuliffe, C. D. Amount and movement of water-soluble sulfur in Minnesota soils. 1942. [Unpublished master's thesis. Copy on file University of Minnesota, St. Paul.]

Although in any extensive work regarding organic matter in soils, sulfur has been mentioned as a constituent, the only study found dealing with it specifically is one by Vinokurov (8) made on the organic sulfur of some Russian soils.

MATERIALS AND METHODS

The soils used in this study are representative of three of the great soil groups found in Minnesota; chernozems from the southwestern, black prairie soils from the south-central, and podzols from the northern portions of the state (fig. 1). Some of the samples of the podzols are from the Taylor-Nebish area

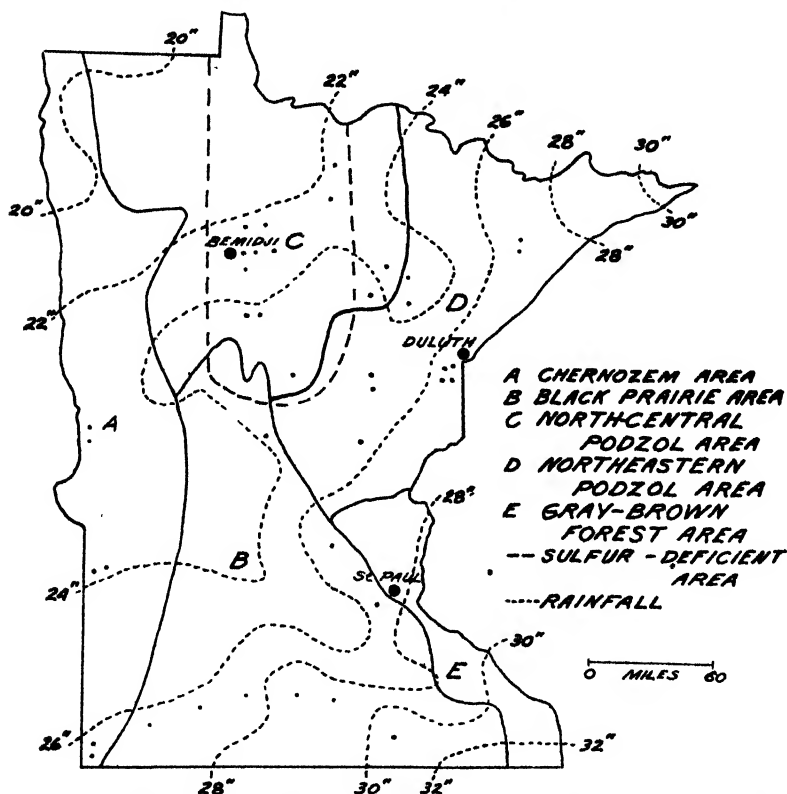


FIG. 1. MAP OF MINNESOTA, SHOWING RAINFALL, SOIL GROUPS, AND SAMPLING SITES

and the others from the Iron River—Milaca area (fig. 1). The former soils are in the north-central part of the state, the latter in the northeastern. The terms "north-central podzols" and "northeastern podzols" will be used to designate these soils in subsequent discussions.

Some of the soil samples were collected during soil surveys of the various counties and the others in connection with research studies now in progress in the Division of Soils. They range in texture from sands to clay loams. Although the soils do not all have the same parent material, this is of little significance, since this study is confined chiefly to the A horizon of the soil profile.

For the determination of total organic sulfur, 5- or 10-gm. samples, depending on the amount of organic matter, of finely ground soil were leached with distilled water, then with 1 per cent hydrochloric acid, and finally with distilled water until no chloride was present in the leachate. The soil was transferred to a beaker and oxidized with hydrogen peroxide, filtered through Chamberland filter tubes, and the sulfur precipitated with barium chloride. In order to eliminate the sulfuric acid carried as an impurity in the hydrogen peroxide, the peroxide was distilled in vacuum, which reduced the strength from 30 to about 15 per cent. This is a modification of the method described by Vinokurov (8), who used sodium chloride and alcohol rather than water and acid to leach the soil.

Humus sulfur was determined by leaching 50 gm. of soil with 500 ml. of distilled water, 500 ml. of 1 per cent hydrochloric acid, and again with 500 ml. of distilled water. The soil was transferred to bottles and shaken several times over a period of 3 days with 1 liter of 4 per cent ammonium hydroxide to peptize the humic material. After standing, the supernatant liquid containing the humic material was siphoned off and passed through Chamberland filter tubes to remove the suspended clay. A 500-ml. aliquot was taken to dryness and fused with magnesium nitrate (4). Sulfur was determined on the water extract of the fused material.

Sulfate sulfur was precipitated with barium chloride after the water and acid leachate from the 50 gm. of soils used for determining humus sulfur had been concentrated in a Kjeldahl flask and filtered.

In the determination of total sulfur 5 gm. of soil was fused with anhydrous sodium carbonate in platinum crucibles. The sulfur was precipitated from the filtered water extract of the melt (6). It was found advantageous to remove the silica rather than precipitate the barium sulfate in the presence of silica.

The amount reported as nonsulfate sulfur was found by subtracting the value for organic sulfur plus sulfate sulfur from the total sulfur.

Total carbon was determined by dry combustion in an oxygen stream, total nitrogen by the Kjeldahl method, and carbonate carbon by the gravimetric method of the A.O.A.C. (4). Figures for carbonate carbon were subtracted from total carbon and are not reported in the tables. Organic matter was determined by treatment of soil with 30 per cent H_2O_2 and the loss in weight taken as the organic matter.

EXPERIMENTAL RESULTS

Humus fraction

In any study pertaining to the organic matter of the soil, the present conception regarding the origin and composition of the humus fraction must be considered. Humus should not be regarded as a single compound or a group of isolated compounds in the soil, but rather as a state of matter. Both plant and animal residues incorporated in the soil become a source of humus. These residues undergo physical and chemical changes as the result of climatic and biological influences. The biological activity is probably the most important

in the process of humification. The soil organisms break down the complex residues and also synthesize a protoplasmic complex from the simpler compounds. The organic fraction is thus in a constant state of flux. Numerous investigations have succeeded in isolating various specific substances from the soil which would prove the existence of such a cycle (9).

Most of our information regarding the chemical nature of humus is based on that fraction of soil organic matter which is soluble or peptized in dilute alkali solutions. Either sodium or ammonium hydroxide of 2 to 4 per cent has been most widely used. The alkali extract from leached soil may be separated into two fractions by treatment with a mineral acid. These fractions are a dark brown flocculate and a light straw to dark brown liquid. The color of the flocculate depends on the concentration and kind of alkali as well as the kind of soil used. The color of the liquid depends on the ratio of soil to liquid during extraction and on the kind of soil used. The flocculate as a rule has been termed "humic acid" or "alpha humus." The liquid has generally been referred to as the "nonhumic fraction." The authors suggest the term "beta-humus fraction" for the liquid. This term, like "alpha humus," serves only to designate, without an attempt to be descriptive, one of the two fractions of alkali extract resulting when humus is treated with a mineral acid. It is well known that both fractions may be further separated.

The humus sulfur in the chernozems and black prairie soils (table 1) is fairly constant. The lowest and highest amounts are 32 and 94 p.p.m. respectively, with an average of 58 p.p.m. for the chernozems and 59 p.p.m. for the black prairie soils. Only a trace of humus sulfur was found in the C horizon of the three samples examined. The relationship of humus sulfur to nitrogen is shown as a ratio (table 2). It will be observed that the ratios are fairly constant. They are on an average slightly wider in the chernozems. Humus sulfur accounts for 10 to 15 per cent of the total sulfur in the chernozems and black prairie soils, with the exception of samples 10 and 15. In general, a slightly higher percentage of sulfur in the humus form is found in the black prairie soils.

In the podzols the amounts of humus sulfur are extremely variable, the range being from 3 to 53 p.p.m. (table 1). The average amount of humus sulfur is higher in the northeastern than in the north-central podzols. The nitrogen-humus-sulfur ratio, although variable, is interesting in that with the great range in the amounts of nitrogen and humus sulfur, and the small amounts of the latter present, most of the ratios fall in a narrow range (table 2). In the northeastern podzols eight of the eleven samples fall within the 20 to 40 range. The ratios are more widely separated in the north-central podzols. In more than half of the podzol samples 10 to 20 per cent of the sulfur is in the humus form.

It has been pointed out by Evans⁴ that most of the humus sulfur is found in the beta-humus fraction. This would indicate that humus sulfur, which is soluble in dilute alkali and not flocculated by acids, is in the final stages of decomposition and would soon become completely mineralized.

⁴ Evans, C. A. Humus sulfur and phosphorus in Minnesota soils. 1943 [Unpublished doctor's thesis. Copy on file University of Minnesota, St. Paul.]

TABLE 1

Analytical data of chernozem, podzol, and black prairie soils of Minnesota

SOIL NUMBER	SOIL TYPE	DEPTH	pH	ORGANIC MATTER	C	N	SULFUR				
							Total	Organic	Sulfate	Non-sulfate	Humus
							p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Chernozems											
1	Barnes silt loam	0-8	7.5	4.531	4.165	.339	523	405	13	105	60
2	Barnes silt loam	0-12	6.6	5.012	4.312	.383	552	425	13	116	56
3	Barnes silt loam	0-12	6.1	4.176	3.018	.275	434	294	16	124	50
4	Moody silt loam	0-12	6.0	5.990	4.369	.368	516	411	15	90	68
5	Moody silt loam	0-12	5.4	3.140	2.990	.280	493	345	17	131	66
6	Moody silt loam	0-8	6.5	3.050	2.649	.242	412	280	9	123	47
Average.				4.316	3.583	.314	488	360	14	115	58
Black prairie soils											
7	Clarion silt loam	0-12	6.0	4.166	3.444	.293	463	314	12	137	65
8	Clarion silt loam	0-12	6.8	3.668	3.109	.271	446	298	16	132	64
9	Clarion silt loam	0-8	5.6	4.502	3.500	.303	438	339	14	85	60
10	Clarion silt loam	0-12	4.7	4.929	3.742	.334	441	324	26	91	94
11	Clarion silt loam	0-12	5.3	5.014	4.516	.350	669	428	25	216	82
12	Carrington silt loam	0-12	4.9	2.616	2.079	.184	277	216	22	39	42
13	Waukegan silt loam	0-14	5.6	4.495	3.546	.287	439	341	13	85	51
14	Clarion loam	0-20	5.2	2.934	2.951	.243	439	299	45	95	47
15	Hubbard sandy loam	A horizon	4.8	1.605	1.979	.165	347	220	14	113	32
Average. ..				3.769	3.207	.270	440	309	20	110	59
C horizon of chernozem and black prairie soils											
1'	Barnes silt loam						169	11	24	134	Tr.
6'	Moody silt loam						146	27	23	96	Tr.
9'	Clarion silt loam						151	27	12	112	Tr.
Average.....							155	21	19	115	
Podzols of the northeastern region											
16	Omega loamy fine sand	0-6	4.5	0.321	0.472	.045	48	18	2	28	14
17	Omega loamy fine sand	A horizon	4.8	2.544	2.102	.109	107	77	3	27	12
18	Omega loamy sand	A horizon	5.4	0.702	0.941	.062	100	29	1	70	16
19	Omega loamy sand	A horizon	4.4	1.775	1.353	.061	82	30	7	45	11
20	Hibbing very fine sandy loam	0-6	4.1	1.630	1.920	.129	123	78	19	26	53

TABLE 1—Continued

SOIL NUM- BER	SOIL TYPE	DEPTH	pH	ORGAN- IC MATTER	C	N	SULFUR				
							Total	Organ- ic	Sulfate	Non- sulfate	Humus
							p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
<i>Podzols of the northeastern region—Continued</i>											
21	Hibbing very fine sandy loam	A horizon	4.5	0.952	1.066	.088	131	38	9	84	24
22	Swan fine sandy loam	A horizon	5.2	0.746	0.543	.056	128	33	3	92	12
23	Onamia fine sandy loam	A horizon	5.5	1.030	1.454	.103	114	74	6	34	20
24	Nashwauk stony loam	0-6	3.9	0.829	0.877	.029	74	31	10	33	11
25	Cloquet stony sandy loam	0-4	3.7	2.143	2.078	.152	118	81	29	8	37
26	Cloquet stony sandy loam	0-6	4.5	1.764	1.821	.139	86	64	5	17	43
Average.				1.312	1.329	.088	101	50	8	42	23

Podzols of the northcentral region

27	Cass Lake fine sand	A horizon	5.2	1.022	1.234	.062	127	48	3	66	9
28	Langor gravelly sand	A horizon	4.8	0.536	0.692	.064	96	15	..	81	6
29	Nymore loamy sand	A horizon	5.1	1.315	1.470	.091	77	59	7	11	14
30	Menahga loamy sand	A horizon	5.2	1.325	0.723	.050	73	23	6	44	13
31	Marquette loamy fine sand	0-6	5.1	0.431	0.654	.039	51	15	1	35	8
32	Nebish loamy fine sand	A horizon	6.2	0.887	0.936	.077	81	53	1	27	16
33	Nymore loamy fine sand	0-6	5.3	0.810	0.773	.071	96	67	7	22	8
34	Hazelwood loamy fine sand	A horizon	5.4	0.579	0.759	.080	132	34	20	78	3
35	Todd sandy loam	A horizon	5.2	0.183	0.326	.034	49	11	6	32	9
36	Rockwood sandy loam	A horizon	5.4	0.138	0.315	.046	32	12	6	14	9
37	Rockwood sandy loam	0-6	5.0	2.181	2.203	.154	144	86	7	51	21
38	Taylor clay loam	A horizon	6.3	0.772	0.978	.078	99	55	2	42	4
39	Taylor silt loam	A horizon	5.9	0.539	0.532	.050	82	40	2	40	9
Average.				0.824	0.819	.069	88	40	6	43	10

TABLE 2
Sulfur relationships and distribution in chernozem, podzol, and black prairie soils of Minnesota

SOIL NUMBER	C N	C ORGANIC S	N ORGANIC S	N HUMUS S	PERCENTAGE OF TOTAL SULFUR AS			
					Inorganic		Organic	
					Sulfate	Non-sulfate	Total organic	Humus
Chernozems								
1	12.2	102.9	8.3	56.5	2.5	20.1	77.4	11.5
2	11.2	101.4	9.0	68.3	2.3	20.8	76.9	10.1
3	10.9	102.6	9.3	55.0	3.7	28.6	67.7	11.5
4	11.8	106.3	8.9	54.1	2.9	17.5	79.6	13.1
5	10.6	86.6	8.1	42.4	3.4	26.6	70.0	13.3
6	10.9	94.6	8.6	51.4	2.2	29.8	68.0	11.4
Average ..	11.4	99.1	8.7	54.6	2.8	23.9	73.3	11.9
Black prairie soils								
7	11.7	109.6	9.3	45.0	2.6	29.6	67.8	14.0
8	11.4	104.3	9.0	42.3	3.6	29.6	66.4	14.3
9	11.5	103.2	8.9	50.5	3.2	19.4	80.6	13.6
10	11.2	115.4	10.3	35.5	5.9	20.7	73.4	21.3
11	12.9	105.5	8.1	42.6	3.7	32.4	63.9	12.2
12	11.2	96.2	8.5	43.8	7.9	14.2	77.9	15.1
13	12.3	103.9	8.4	56.2	2.9	19.5	77.6	11.6
14	12.1	98.6	8.1	51.7	10.2	21.6	68.2	10.7
15	11.9	89.9	7.5	51.5	4.0	32.6	63.4	9.2
Average .	11.8	103.1	8.7	46.6	4.9	24.4	71.0	13.4
C horizon samples								
1'					6.5	79.3	14.2	0
6'					18.4	65.7	15.7	0
9'					8.0	74.2	17.8	0
Average					11.0	73.1	15.9
Northeastern podzols								
16	10.4	262	25.0	31.7	4.2	58.3	37.5	29.1
17	19.2	272	14.1	90.4	2.8	25.3	71.9	11.2
18	15.1	324	21.3	38.1	1.0	70.0	29.0	16.0
19	22.1	451	20.3	37.2	8.5	55.0	36.5	13.4
20	14.8	246	16.5	24.2	15.4	21.2	63.4	43.0
21	12.1	280	23.1	36.2	6.8	64.1	29.1	18.3
22	9.7	164	16.6	46.4	2.4	71.8	25.8	9.3
23	14.1	196	13.9	51.8	5.3	29.8	64.9	17.5
24	30.2	282	9.4	27.2	13.6	44.6	41.8	14.8
25	13.6	256	18.7	22.9	24.5	6.9	68.6	31.3
26	13.1	284	21.7	32.1	5.8	19.8	74.4	50.0
Average ...	15.1	265.8	17.6	38.2	7.9	41.6	49.5	22.7

TABLE 2—*Continued*

SOIL NUMBER	$\frac{C}{N}$	$\frac{C}{\text{ORGANIC S}}$	$\frac{N}{\text{ORGANIC S}}$	$\frac{N}{\text{HUMUS S}}$	PERCENTAGE OF TOTAL SULFUR AS			
					Inorganic		Organic	
					Sulfate	Non-sulfate	Total organic	Humus
<i>Northcentral podzols</i>								
27	19.9	257	11.7	68.8	2.4	51.9	37.7	7.0
28	10.8	461	42.6	106.6	...	84.3	15.7	6.2
29	16.1	249	15.4	65.0	9.1	14.3	76.6	18.1
30	14.4	314	21.7	38.4	8.2	60.3	31.5	17.8
31	16.7	436	26.0	48.7	1.9	68.7	29.4	15.6
32	12.1	176	14.5	48.1	1.2	33.4	65.4	19.7
33	10.8	115	10.5	88.7	7.3	22.9	69.8	8.3
34	9.4	223	23.5	266.6	15.1	59.1	25.8	2.3
35	9.5	296	30.9	37.7	12.2	65.4	22.4	18.3
36	6.8	262	38.3	51.1	18.8	43.7	37.5	28.1
37	14.3	256	17.9	73.3	4.8	35.5	59.7	14.5
38	12.5	177	14.1	19.5	2.0	42.5	55.5	4.0
39	10.6	133	12.5	55.5	2.4	48.8	48.8	10.9
Average...	11.8	204	17.2	69.0	6.8	48.8	45.4	11.3

The nitrogen-humus-sulfur ratios are generally wider in the chernozems and north-central podzols than those in the black prairie soils and the northeastern podzols. The nitrogen-organic-sulfur average ratio of chernozems and black prairie soils is identical, and there is only a slight variation in the podzols.

Thus whenever soils of similar texture have identical nitrogen-organic-sulfur ratios the one receiving the greater rainfall will have a higher rate of humification. The percentages of sulfur as humus sulfur and as sulfate sulfur are, on the average, less in regions of lower rainfall when compared to a similar type of soil receiving a greater rainfall. This also brings us to the conclusion that the rate of humification and the amount of humus sulfur are influenced by climatic conditions and further that humus sulfur is approaching complete mineralization.

Total organic sulfur

The sulfur present in the filtrate following the digestion of leached soils with hydrogen peroxide constitutes the total organic sulfur. This includes the humified portion as well as undecomposed organic residues. In the chernozems and black prairie soils (table 1) the amounts of organic sulfur range from 216 to 428 p.p.m. The chernozems have on the average slightly higher amounts than do the black prairie soils. This would be expected, since the chernozems are developed under conditions of lower rainfall, which is more favorable for the accumulation of organic matter. The organic sulfur of the C horizon of these soils is probably due to downward movement of organic matter by mechanical means and to the penetration of some plant roots.

Both the carbon-organic-sulfur ratios and the nitrogen-organic-sulfur ratios are about the same for chernozem and black prairie soils. The carbon-organic-sulfur ratio is approximately 100 and the nitrogen-organic-sulfur ratio 8.7 (table 2). It should be noted that the individual ratio for each sample does not vary greatly from the average. In the percentage distribution of organic sulfur (table 2) a minimum of 63 per cent of the total sulfur is in this form.

As in the case of humus sulfur the amounts of total organic sulfur in the podzols are subject to wide variation, the range being from 11 to 86 p.p.m. With the great difference in the amounts of total organic matter, this variation might be expected. For example, two samples (Nos. 16 and 17) having the same texture show a difference ranging from 0.32 to 2.5 per cent organic matter.

In the majority of cases, the carbon-organic-sulfur and the nitrogen-organic-sulfur ratios are more than twice as great as those in the prairie type soil. The average nitrogen-organic-sulfur ratio for podzols is approximately 17 as compared to 8.7 for the prairie type soils. In only a few cases do the ratios for the podzols approach those of the prairie soils. The percentage of sulfur in the organic form is definitely lower in the podzols than in the prairie type soils (table 2). For the podzols it will average less than 50 per cent of the total sulfur.

The most significant figure on organic sulfur is the nitrogen-organic-sulfur ratio. When sulfur is added to the soil there are several possibilities as to its fate. As the sulfate ion, it would leach from the soil, be held in some manner by the clay complex, or combine as an insoluble mineral compound. As organic sulfur, it would occur as a constituent of plant or animal protein. (Other sulfur compounds of organisms are insignificant except in a few cases.) The nitrogen-organic-sulfur ratios of the chernozems and black prairie soils vary only within narrow limits, but in the podzols this variation is wider. Since the ratio is wider in the podzols than in the prairie soils there is a possibility that this ratio may be used as a criterion for the identification of sulfur-deficient soils. Further work on this phase of the problem is now in progress.

In only seven of the twenty-four samples of podzols is the organic sulfur less than 30 per cent of the total sulfur, and in the prairie types it accounts for more than 60 per cent of the total sulfur. The organic matter therefore serves as a reservoir for sulfur as well as for the other nutrients that are made available during the process of humification and of mineralization. The carbon-organic-sulfur ratio follows the same trend as the nitrogen-organic-sulfur ratio.

Our data are not in general agreement with those of Vinokurov (8). Slightly different methods were used in leaching the soils in the two studies, but whether or not this slight difference in procedure could cause the disagreement was not investigated. In his conclusion, Vinokurov says that the amounts of organic sulfur are insignificant. The greatest amount reported for a Russian soil (table 3) is 23 p.p.m. for a solonetz. Some of the Minnesota podzols (table 1) are this low also. Even in these podzols that have a low amount of organic sulfur, however, this constitutes over 20 per cent of the total sulfur, whereas in the prairie types sulfur in this form is over 60 per cent of the total. In

Minnesota soils the chernozems are highest in organic sulfur, as would be expected. Vinokurov found the Russian chernozems to be lowest in organic sulfur.

In some Russian soils (for example, the first podzol reported in table 3) the organic sulfur increases in the lower A and the upper B horizons. In other cases it is about equal in both horizons, and in one chernozem it decreases with

TABLE 3
Sulfur content of organic fractions of various Russian soils
Analytical data of Vinokurov (8)

SOIL	HORIZON	DEPTH	CARBON	SO ₂ IN ORGANIC MATTER	ORGANIC SULFUR
		cm.	per cent	per cent	p.p.m.
Strongly podzolized	A	0-11	2.10	.0022	8.8
	A	12-22	0.42	.0038	15.2
	B	35-45	0.29	.0038	15.2
Turf podzol	A	0-10	1.48	.0036	14.4
	A	10-16	1.54	.0038	15.2
	AB	18-28	1.25	.0023	9.2
Dark gray podzol	A	0-12	3.80	.0028	11.2
	A	13-21	3.25	.0046	18.4
Leached chernozem	A	0-10	4.83	.0024	9.6
	A	18-28	4.96	.0020	8.0
	AB	36-46	2.97	.0024	9.6
Strongly (extra) leached chernozem	A	0-10	4.55	.0025	10.0
	A	15-25	3.63	.0029	11.6
	AB	35-45	2.40	.0023	9.2
Ordinary chernozem	A	0-10	2.65	.0029	11.6
	A	10-20	3.02	.0013	5.2
Southern solonetzic	A	0-10	2.16	.0049	19.6
	AB	26-44	1.36	.0055	22.0
Chestnut soil	A	0-10	0.88	.0052	20.8
	AB	10-26	0.60	.0028	11.2
Gray soil	A	0-7	1.11	.0058	23.2
Solonetzic	B	12-17	0.73	.0047	18.8
Solonetz	B	18-23	0.60	.0027	10.8

depth. The organic sulfur was not determined on the B horizon of Minnesota soils, but where determinations were made on samples from different layers of the A horizon of a given profile, the organic sulfur was found to be greater at the surface and to decrease along with a decrease in organic matter with an increase in depth.

The carbon-organic-sulfur ratio is widest in the leached chernozems according to Vinokurov. The following tabulation compares the average data for Russian soils (table 3), and for Minnesota soils (table 1):

	C	N	ORGANIC S	C	N
	per cent	per cent	p.p.m.	ORGANIC S	ORGANIC S
6 Minnesota chernozems.....	3.58	.314	360	99	8.7
9 Minnesota black prairie soils.....	3.20	.270	309	103	8.7
3 Russian chernozems ..	4.01		10	3855
11 Minnesota podzols.	1.32	.088	50	265	17.6
13 Minnesota podzols.81	.069	40	204	17.2
3 Russian podzols....	2.46	.	11	2157	.

For Minnesota soils the carbon-organic-sulfur ratio is widest in the podzols. There is a direct relationship between the amounts of carbon and nitrogen and the amount of organic sulfur. Since organic sulfur of the soil would occur almost entirely as protein it would be of interest to know the nitrogen content of the Russian soils.

Vinokurov asserts that changes in the cellulose and hemicellulose content of the soil vary directly with changes in the organic sulfur, whereas changes in the ligno-protein complex vary indirectly with changes in the organic sulfur. The data for Minnesota soils indicate a direct variation of both carbon and nitrogen with humus sulfur as well as with total organic sulfur.

Vinokurov points out that the findings indicate that organic sulfur is a factor of climatic order. The humus sulfur and, to some extent, the total organic sulfur in Minnesota soils are influenced by climate.

Nonsulfate sulfur

The values for nonsulfate sulfur were obtained by subtracting the sulfate sulfur plus the organic sulfur from the total sulfur. Table 1 shows the nonsulfate sulfur to vary from 85 to 137 p.p.m. in the A and C horizons of the prairie soils (samples 11 and 12 show an extreme range and are not typical of the average). In the podzol soils (table 1) the amounts of nonsulfate sulfur are extremely variable. On the average it is less than half the amount found in the prairie soil types.

The nonsulfate sulfur as defined could exist in two forms, one as insoluble sulfur compounds which would not be broken down under methods used in determinations of humus or organic sulfur, and the other as sulfur adsorbed or held in some manner by the clay complex (7). Kjeldahl determinations were made on several soil residues after treatment of the soil with hydrogen peroxide. No nitrogen was found in the samples, and it is apparent that the protein sulfur has been oxidized.

An examination of table 1 shows that the chernozems and black prairie soils, which have approximately the same clay content, carry similar amounts of the

nonsulfate sulfur, whereas the light-textured podzols contain much less non-sulfate sulfur. In subsoils (table 2) more than 70 per cent of the total sulfur is in the nonsulfate form.

Sulfate sulfur

The results obtained for sulfate sulfur merely serve to confirm the fact that this fraction is extremely variable. The greatest amounts are found in the chernozems and black prairie soils.

The percentage of sulfur as sulfate sulfur is higher in the podzols than in the chernozems and the black prairie soils. This is probably due to a more rapid mineralization of the organic matter in the lighter-textured soils.

SUMMARY

Total sulfur, total organic sulfur, the humus fraction of organic sulfur, sulfate sulfur, carbon, and nitrogen were determined on 39 samples of the podzol, chernozem, and black prairie soils of Minnesota.

The term "beta humus" is suggested as the designation for the liquid fraction of the alkali humus extract after flocculation of alpha humus with an acid.

Humus sulfur appears to be contained in that portion of the organic matter which is in an advanced stage of mineralization. The amount appears to be affected by climatic conditions.

Both humus and total organic sulfur were higher in the chernozems and the black prairie soils than in the podzols. The organic matter acts as a reservoir for sulfur as well as other mineral nutrients.

A direct correlation exists between the amounts of humus sulfur and the amounts of nitrogen and carbon in the soil. A direct correlation also exists between the amounts of total organic sulfur and the amounts of nitrogen and carbon. In the chernozems and black prairie soils the correlation is more apparent than in the podzolic soils. The relationship of nitrogen to organic sulfur may be useful as a criterion for the estimation of sulfur deficiency.

The amounts of water-soluble sulfur in Minnesota soils were found to be variable. In this respect the results are in agreement with the findings of other investigations for soils of this region.

REFERENCES

- (1) ALWAY, F. J. 1927 Detection of sulfur deficiency of soils by means of plants. *Proc. First Internatl. Cong. Soil Sci.* 3: 590-618.
- (2) ALWAY, F. J., MARSH, A. W., AND METHLEY, W. J. 1937 Sufficiency of atmospheric sulfur for maximum crop yields. *Proc. Soil Sci. Soc. Amer.* 2: 229-238.
- (3) AMES, J. W., AND BOLTZ, G. E. 1916 Sulfur in relation to soils and crops. *Ohio Agr. Exp. Sta. Bul.* 292: 221-256.
- (4) ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS 1940 Official and Tentative Methods of Analysis, ed. 5. Washington, D. C.
- (5) BROWN, P. E., AND KELLOGG, E. H. 1915 Sulfur and permanent soil fertility in Iowa. *Jour. Amer. Soc. Agron.* 7: 97-108.

- (6) MARBUT, C. F. 1935 Atlas of American Agriculture, part 3. U. S. Government Printing Office, Washington, D. C.
- (7) MATTSON, S. 1927 Anionic and cationic adsorption by soil colloidal materials of varying $\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ Ratio. *First Internatl. Cong. Soil Sci. Proc. and Papers* 2: 199-211.
- (8) VINOKUROV, M. A. 1937 The content of sulfur in the organic part of soil and a method for its extraction. *Pedology* 32: 493-504.
- (9) WAKSMAN, S. A. 1938 Humus, ed. 2. The Williams & Wilkins Co., Baltimore, Md.

EFFECT OF HIGH CONCENTRATIONS OF SODIUM, CALCIUM, CHLORIDE, AND SULFATE ON IONIC ABSORPTION BY BEAN PLANTS

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Salt accumulations in saline soils are usually a mixture of the components of several salts, but in certain areas a given cation or anion may predominate (23, 25). In many regions subject to salinization, sodium is the main cation found in the soil solution; in other regions calcium, or more rarely magnesium, is preponderant. The anions present in such soil solutions are frequently found to be mostly chloride, but the sulfate ion may also be present in excessive amounts. Even nitrate ions occasionally accumulate. The variation found in the proportions of the ions is practically infinite. So far as experimentation involving the influence of various salines on plant growth is concerned, the study of a particular mixture of salts becomes virtually an isolated case when the results obtained are referred to field conditions. A more fundamental evaluation of the effects of salinity is possible if the influence of each component is studied separately before an attempt is made to interpret the effects of various mixtures of salts on plant growth.

It is well known that the effect of sodium on flocculation of soil colloids is quite different from that of calcium, but relatively little information is available concerning the effect of high concentrations of Ca^{++} vs. Na^+ or Cl^- vs. SO_4^{--} on root membranes and, hence, on the uptake of the essential nutrient elements.

In some studies the investigators have subjected plants to high concentrations of chloride vs. sulfate salts, but the proportionality of Ca^{++} , Mg^{++} , and Na^+ was also varied among the different concentrations of the chloride and the sulfate solutions (8, 9, 15, 22). In such studies any specific reactions on the part of the plant could be assigned only to the effect of chloride vs. sulfate, and the experimental design did not permit a segregation of the effect due to variation in the proportion of the cations.

In order to evaluate quantitatively the specific effect of high concentrations of sodium, calcium, chloride, and sulfate on ionic absorption, an experiment was designed in which NaCl , CaCl_2 , and Na_2SO_4 were separately added to a control nutrient solution in increments of one atmosphere osmotic pressure up to and including four atmospheres. Dwarf red kidney beans were grown as the experimental plant.

Expressing the concentration of the culture solutions in terms of osmotic pressure was regarded as most logical. There is an appreciable body of data

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(7, 10, 14, 15, 16, 22, 23) to show that plant growth is closely correlated with the total osmotic pressure of saline culture solutions. Since osmotic pressure is an explicit thermodynamic property of a solution, the energetics of water absorption by plants is definitely conditioned by this property. Although total plant growth is regarded as a function of the total osmotic pressure of the substrate [assuming the osmotically active substances are not toxic *per se* (11)], it would be expected that absorption of a given ion should correlate most closely with the concentration of that ion in the culture solution. Certainly the absorption of a given ion is conditioned by the presence of other ions in the solution. This effect is usually referred to as "antagonism." Inasmuch as it is impossible to evaluate this effect in precise quantitative terms, it is necessary to consider the data on absorption in terms of the known, imposed, independent variables. Thus for the following discussion the accumulation of an ion in the plant material is interpreted as a function of the equivalence concentration of that ion in the substrate solution in all cases where the concentration of that ion was varied.

TABLE 1
*Composition of the base nutrient solution**

Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ⁻⁻	H ₂ PO ₄ ⁻	NO ₃ ⁻
5.9	2.7	2.1	m.e./l.			1.5	7.0
			4.1	1.8	4.3		
			p.p.m.				
118	33	47	158	64	200	148	434

(0.5 p.p.m. of B, Mn, and Fe; Zn, as impurity in salts)

* Total osmotic pressure, 0.5 atmosphere.

Although reference will be made to several theories of permeability as they relate to the data of this experiment, the authors wish to emphasize the inadequacy of the available theories for explaining all of the observed effects of one ion upon the absorption of other ions. The data reported herein only tend to corroborate the evidence that salt absorption involves an extremely complex series of interrelated processes.

The composition of the base nutrient solution is shown in table 1. The component salts of this nutrient were added to Riverside tap water, together with 2 m.e./l. of the total nitrate added as HNO₃, giving a pH of about 5.7. Plants grown in cultures of this solution were regarded as the controls, and the other experimental treatments consisted of adding NaCl, CaCl₂, or Na₂SO₄ separately to the solution so that the total osmotic pressure was increased by each of these salts to the extent of 1, 2, 3, and 4 atmospheres.

By adding various amounts of NaCl, of CaCl₂, and of Na₂SO₄ to the base nutrient solution and determining the resultant freezing-point depression, it was possible to derive the functional relationship between osmotic pressure and milliequivalents per liter of each added salt.

For the conditions of this experiment, i.e., technical salts added to a base nutrient solution, figure 1 illustrates the relationship between milliequivalents of salt per liter and osmotic pressure expressed in atmospheres. These data agree fairly closely with similar data from the International Critical Tables, and it is assumed that the slight differences were caused by the interaction of the added salt with one or more constituents of the base nutrient solution and by impurities in the technical salts used.

The technique for growing the plants in aerated solution culture (6), the rate at which the solutions were brought to the predetermined concentrations of salt, and the fractionation of plant parts at the time of harvest were reported

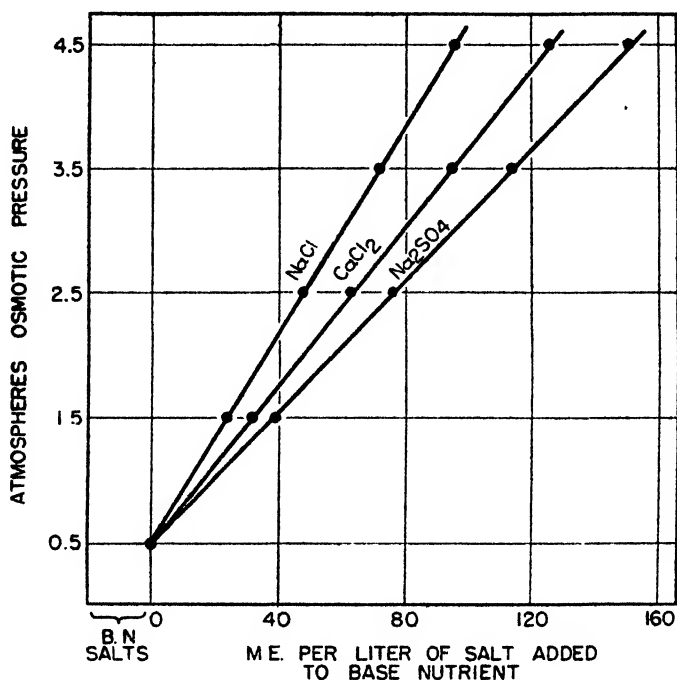


FIG. 1. RELATIONSHIP BETWEEN MILLIEQUIVALENTS OF SALT PER LITER AND OSMOTIC PRESSURE, EXPRESSED IN ATMOSPHERES

in a previous paper (11). The appearance of the tops and roots of these same plants also was described (11). Only the dry weights of the plants, therefore, are repeated herein because of their importance in the interpretation of the present data.

ANALYTICAL METHODS

One- to two-gram samples of plant material were ashed in a muffle at low dull-red heat (500–550° C.). The resulting ash was dissolved in dilute HCl, and suitable aliquots were taken for analysis. In general, A.O.A.C. methods (1) were followed. Calcium was precipitated as the oxalate and titrated with potassium permanganate. Sodium was determined by the uranyl zinc acetate

method, following certain precautions suggested by Broadfoot and Browning (2). Potassium was determined by precipitation with cobaltinitrite and titrated with potassium permanganate. Chloride was determined by titration with AgNO_3 , and sulfate was precipitated as BaSO_4 and weighed. Phosphorus was precipitated as phosphomolybdate and titrated. Total nitrogen was determined by a modification of Ranker's (30) method adapted to the micro-Kjeldahl apparatus.

RESULTS

The appearance of the plants after 3 weeks of treatment is shown in figure 2. Detailed morphological observations on these plants together with the effects of magnesium salts have been presented in another paper (11). The most striking feature was the similarity of the plants at isosmotic concentrations of the three different added salts. It should be noted in this connection, however, that these plants were harvested at incipient flowering, and it is possible that differentiating symptoms might have developed during the reproductive phase of growth.

As shown by figure 3, at isosmotic pressures the plant weights were very nearly equal, regardless of which salt was added to the base nutrient solution. The weights of the sodium sulfate plants tended to be the lowest at each osmotic pressure level. Hayward and Long (14) observed a greater depression in growth of tomato plants with Na_2SO_4 than with NaCl as the added salt, particularly at the higher levels of concentration. In a comparison of the effects of NaCl , CaCl_2 , and Na_2SO_4 on the growth of Punjab flax, Hayward and Spurr (17) also observed a greater depression with Na_2SO_4 at any given osmotic pressure than with either of the other two salts. It seems likely that response is conditioned by the species of plant, for Hayward and Long (15) have shown that peach trees are more sensitive to chloride salts than to sulfate salts, and Eaton (8) found that various species of plants differed with respect to the relative toxicity of chloride *vs.* sulfate salts.

Effect of added salts on elemental composition of plants

Calcium. Bean plants usually contain appreciably more calcium than do plants of certain other species, *viz.*, the cereals. It is conceivable, therefore, that calcium absorption by beans would be responsive to wide variations in the concentration of this ion in the growing medium. Despite an increase in the concentration of calcium in the culture solution from 6 m.e./liter to 132, the concentration of calcium in the entire plant increased only from 1.25 m.e./gm. dry weight in the control plants to 2.18 in the plants grown in the highest concentration of calcium chloride. In other words, the most striking feature of calcium uptake was the moderate degree to which calcium concentration in the bean plant was influenced by wide variations in Ca^{++} concentration in the external medium (fig. 4). But the bean plant is characterized by a relatively high concentration of calcium in its tissues. For example, on the basis of milliequivalents per gram of dry matter, the calcium content in the leaves of

the control plants was 3.3 times that of magnesium, about twice that of potassium, and 87 times that of sodium.

Sodium. Collander (5) has concluded from his studies with a number of plant species that "of all the ions, sodium is the one most perfectly excluded

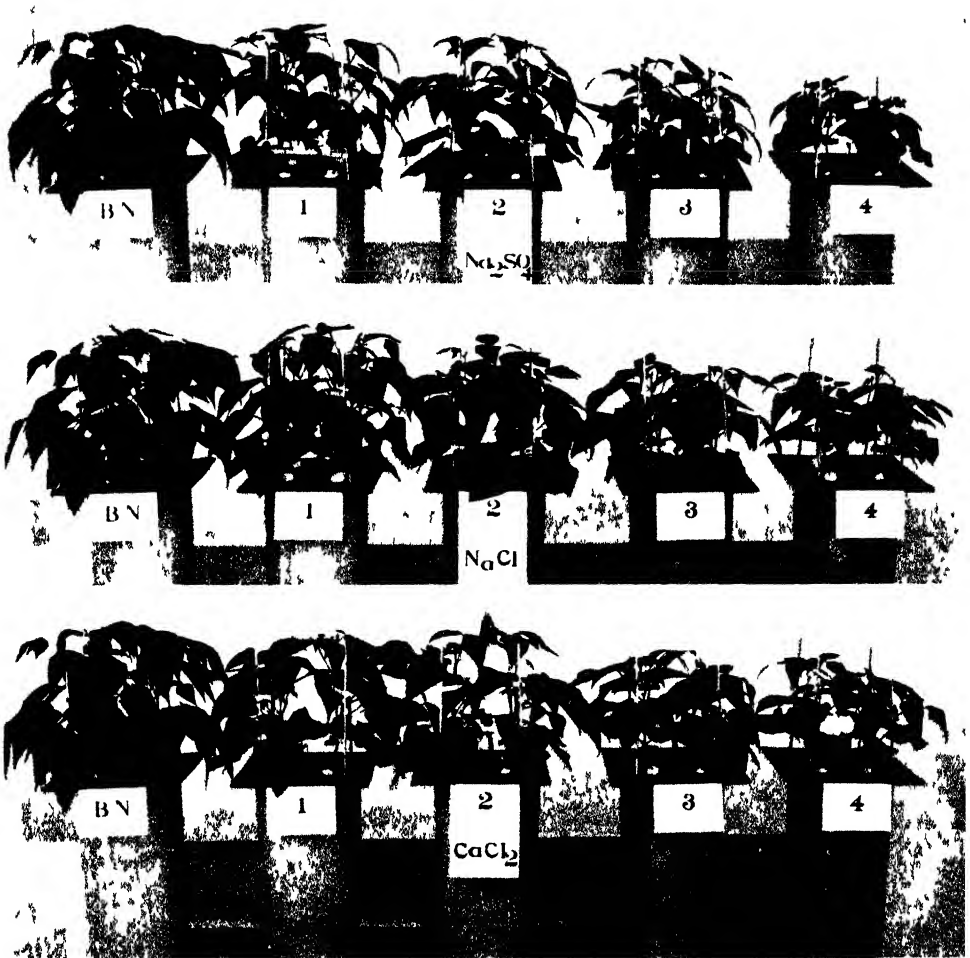


FIG. 2. GENERAL APPEARANCE OF PLANTS AT TIME OF HARVEST, DEC. 29, 1941

Figures on jars stand for atmospheres osmotic pressure of the added salt; B N, base nutrient solution.

by plants." The data with respect to the uptake of sodium by the bean plant have an interesting bearing on this concept. The addition of either NaCl or Na_2SO_4 to the basal nutrient solution resulted in very little change in the sodium content of the leaves, a moderate increase in the concentration of sodium in the stems, and a very striking increase in the roots (fig. 4). It has been assumed

with considerable justification that an analysis of above-ground portions serves as a reliable index as to whether or not a given element has been taken up by a plant. Indeed, in the case of sodium, the assumption would seem to be justifiable, since one would ordinarily expect from the chemical nature of the sodium ion that it would be rather uniformly distributed throughout the plant in the same manner as potassium. Osterhout (26) has noted that the protoplasm of certain cells is able to distinguish electrically between K^+ and Na^+ , and he has succeeded in making an artificial cell which also distinguishes electrically between these ions. This effect appears to be related to the ability of certain cells differentially to exclude sodium. It is possible that this effect is involved in

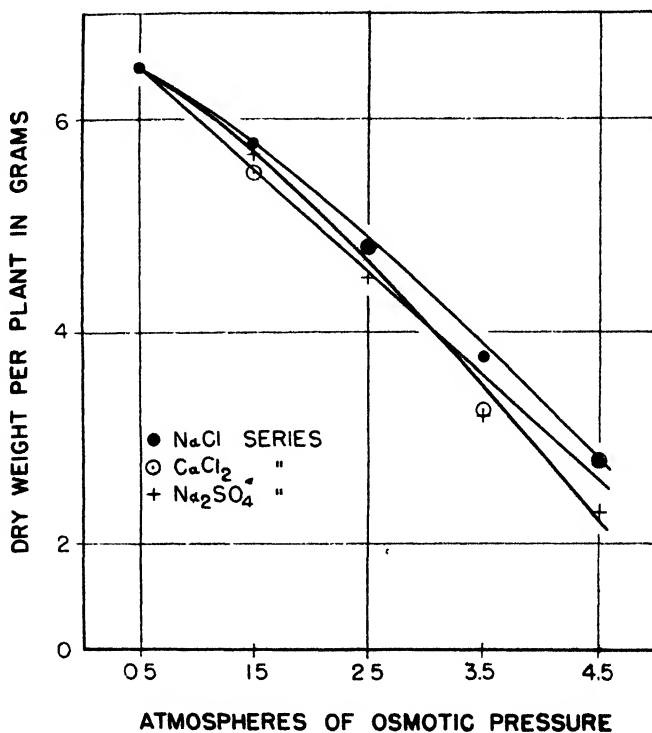


FIG. 3. AVERAGE DRY WEIGHTS OF BEAN PLANTS AT TIME OF HARVEST, DEC. 29, 1941

the mechanism by which sodium accumulated in such relatively high concentrations in the roots of bean plants, despite the slight change in the concentration in the above-ground portions of the plant, particularly the leaves. It is possible that the membranes in the cells of certain extrastelar tissues of the roots may be especially proficient in the exclusion of sodium and operate to withhold it from the vascular system—*e.g.*, the endodermis might act as a restrictive zone in the movement of the sodium ion. By contrast, some species of plants, such as beets, may accumulate rather high concentrations of sodium, and in sugar beet plants the leaves contain *considerably* higher percentages of Na than the roots (19). There is every reason to believe that such an accumu-

lation of sodium as occurs in the roots of bean plants has an effect on the physical behavior of the cells. Numerous studies (3, 18, 24) have established the contrasting effects of Na^+ vs. Ca^{++} upon the physical properties of the cytoplasmic membranes. Chibnall and Channon (4) assert that the "fat-solubility of the calcium salt of phosphatidic acid and the water-solubility of its sodium salt suggest that these phosphatidates may be in part responsible for the alteration in cell permeability which can be brought about by changes in the proportion of

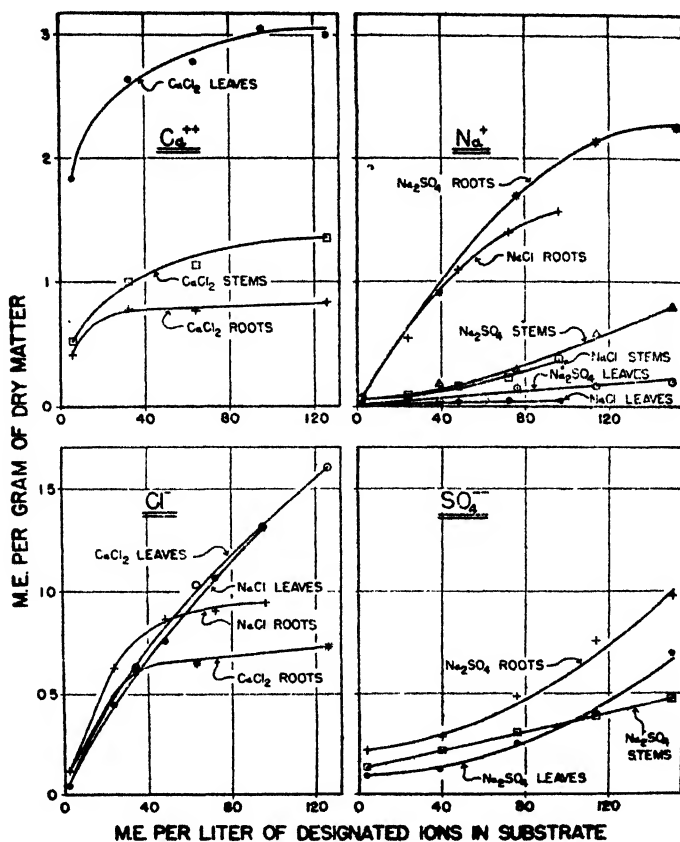


FIG. 4. CONCENTRATIONS OF Ca^{++} , Na^+ , Cl^- , AND SO_4^{--} IN THE VARIOUS PARTS OF BEAN PLANTS AS AFFECTED BY SERIAL INCREASES IN THE CONCENTRATION OF THESE IONS IN THE SUBSTRATE

sodium and calcium ions." Some effects of a high concentration of sodium vs. a high concentration of calcium in bean roots on certain metabolic processes have been discussed in a previous paper (32).

It is known that there is considerable specificity in the behavior of protoplasm from different species, and it is pertinent that Collander (5) has observed that plant species which normally have relatively high concentrations of sodium throughout the plant seem to be the ones that are least sensitive to an increase in sodium concentration in the substrate. Garden beets, sugar beets, *Atriplex*

and other "halophytic" plants are examples of those which may take up large quantities of sodium and are tolerant of relatively high concentrations of sodium in the soil solution. Many salt-sensitive species of plants are known to take up relatively small amounts of sodium (5). It is possible that other species of plants which are characterized by a low proportion of sodium in the tops may likewise have a high proportion of sodium in the roots. Wadleigh and Gauch (32) observed a difference in the status of the nitrogenous constituents of the roots of these same bean plants as conditioned by high concentrations of Na^+ vs. Ca^{++} in the substrate.

Higher concentrations of sodium were found in the plants from cultures with excess Na_2SO_4 than in those from cultures with excess NaCl in the base nutrient solution. This is in contrast with the observation that the concentration of Cl^- in the plants (leaves, especially) of the NaCl series was about twice as high as that of SO_4^{--} in the plants of the Na_2SO_4 series (fig. 4). Hayward and Long (14) observed similar relationships in tomato. Raber's (28, 29) electrostatic theory of permeability relating the density of charge on an ion to its effect on protoplasmic permeability postulates that the SO_4 ion, with its double negative charge, would make the absorbing membranes more permeable than the Cl ion, with its single negative charge. This theory appears to hold for the effect of the respective anions on permeability to sodium, but it does not hold with respect to the accumulation of the anions themselves.

It is questionable whether the slightly greater reduction of growth observed in the Na_2SO_4 series of plants, as compared with respective observations on the NaCl series, is in any way related to the higher concentrations of the sodium ion, *per se*, in the dry matter of the former series. For example, the addition of CaCl_2 resulted in very similar growth depression at isosmotic levels, and in this case sodium could not be a causative factor.

Chloride. The concentration of chloride in the culture solution had the same effect on the chloride content of the leaves and stems whether added as the sodium or the calcium salt (fig. 4). There was practically no increase in the concentration of chloride in the roots with any further increase in the concentration of chloride in the solution above 30 to 50 m.e./liter. But the "level" of chloride concentration in the roots of the NaCl plants was definitely higher than that in the roots of the CaCl_2 series. This would seem to be related to two factors: (a) the retention of relatively large amounts of sodium in the roots of the NaCl plants—an accumulation which would have to be balanced by a stoichiometrical amount of anion, in this case, largely chloride; and (b) the fact that the increases in calcium concentration of the substrate above that present in the treatment having one atmosphere of CaCl_2 did not effect an increase in the calcium concentration of the roots, and the trend of chloride concentration in the roots showed a corresponding relationship. In other words, the nature of chloride accumulation in the roots tended to correspond with the trend in absorption of the related cation in a given substrate.

Sulfate. There were exponential increases in the concentration of sulfate in the leaves and roots as the concentration of sulfate in the solution was in-

creased (fig. 4), whereas the increase in the sulfate concentration in the stems was linear. No adequate explanation of these divergent trends was manifest.

Chloride vs. sulfate concentrations in leaves and roots. When NaCl was added to the base nutrient solution, there was a linear relationship with a relatively steep slope between the concentration of chloride in the solution and in the leaves (fig. 4). This trend was quite distinct from the exponential relationship noted for sulfate concentration in the leaves (Na_2SO_4 series, fig. 4) in that the average slope of the latter curve was much less. In fact, there was very little increase in sulfate content of the leaves with an increase of 39 m.e./liter of sulfate in the culture solution, whereas a corresponding increase in external concentration of chloride caused a marked increase in chloride content in the leaves (NaCl series, fig. 4). The evidence indicates that these plants showed a capacity for selective accumulation of Cl^- over SO_4^{--} . Harris *et al.* (12, 13) have noted that different lines of cotton show considerable specificity in their selective accumulation of Cl^- vs. SO_4^{--} and that this specificity is directly inheritable.

The chloride and sulfate concentrations of respective roots showed trends similar to those noted for the leaves, except that the curve of chloride concentration in the roots was asymptotic with the maximum.

It is permissible to make cross-comparisons at isosmotic levels of salt treatments as to the total amount of a given ion absorbed by the plants, since the dry weights of the plants at a given osmotic pressure were statistically homogeneous. It is evident from table 2 that in the absence of excess chloride or sulfate (control plants) considerably more sulfate than chloride was absorbed. The fact that the control culture solution contained 2.5 times as much sulfate as chloride on the equivalence basis, possibly accounted for the aforementioned difference. Yet the plants took up considerably more chloride when this was the anion added in excess than they did sulfate when the latter was the anion in excess. This is probably related to the fact that the mobility of the sulfate ion is less than that of the chloride ion. The double negative charge of the sulfate ion supposedly would have been conducive to higher membrane permeability (28, 29) than would the single charge on the chloride ion. This does not appear to hold for rate of entry of these respective anions.

*Effect of total concentration of solution, in atmospheres osmotic pressure,
on uptake of certain nutrient elements*

The discussion in the preceding section was developed on the basis that the concentration of a given ion in the plant material is a function of the equivalence concentration (milliequivalents per liter) of that ion in the culture solution. This treatment was possible in that ions so considered were varied in concentration in the solutions. Ions constant in concentration in all treatments may not, however, be evaluated in this manner. In view of the fact that plant growth has been found to be very closely correlated with the osmotic pressure of the culture medium, only minor modifications being induced by the qualitative nature of the constituent ions, it is considered that the accumulation of the ions

constant in all cultures may best be interpreted on the basis of the osmotic pressure of these external solutions.

Calcium (in the NaCl and Na₂SO₄ series of plants). The concentrations of calcium in the leaves, stems, and roots of the NaCl and Na₂SO₄ series of plants are plotted in fig. 5. Increasing amounts of NaCl in the solution tend to increase progressively the concentration of Ca⁺⁺ in the leaves and stems, but had little effect on the concentration of Ca⁺⁺ in the roots. Although magnesium was not determined as a routine procedure on all of the samples, it was

TABLE 2

Effect of serial increments (of 1 atmosphere osmotic pressure) of the designated salts on the quantity of certain ions in bean plants

ATMOSPHERES OSMOTIC PRES- SURE OF ADDED SALT	SERIES			SERIES		
	CaCl ₂	NaCl	Na ₂ SO ₄	CaCl ₂	NaCl	Na ₂ SO ₄
	Average m.e. of designated ion absorbed per plant			Average m.e. of designated ion absorbed per plant		
	<i>Calcium</i>			<i>Chloride</i>		
0 (B.N.)	(8.09)	(8.09)	(8.09)	(0.54)	(0.54)	(0.54)
1	10.36	7.20	6.52	3.24	2.74	0.48
2	9.56	6.06	4.43	4.12	3.49	0.38
3	7.33	5.07	3.06	3.58	3.40	0.27
4	6.07	3.72	2.04	3.52	2.99	0.20
	<i>Sodium</i>			<i>Sulfate</i>		
0 (B.N.)	(0.28)	(0.28)	(0.28)	(0.85)	(0.85)	(0.85)
1	0.25	0.84	1.36	0.72	0.77	1.02
2	0.21	1.39	2.27	0.63	0.64	1.42
3	0.16	1.36	2.21	0.48	0.50	1.54
4	0.12	1.24	1.91	0.37	0.37	1.63
	<i>Potassium</i>			<i>Total N</i>		
0 (B.N.)	(8.16)	(8.16)	(8.16)	(20.39)	(20.39)	(20.39)
1	6.09	7.56	7.56	15.42	16.97	18.69
2	5.30	6.18	5.72	13.18	13.41	14.78
3	3.85	4.58	4.10	9.54	10.25	9.73
4	2.71	3.30	2.89	6.52	7.06	5.72

determined in the leaves of the NaCl and Na₂SO₄ plants, and the concentration also was found to increase progressively in the NaCl plants. The increased concentration of calcium and magnesium in the leaves of the NaCl plants was apparently related to the low increase in Na⁺ content concomitant with a pronounced chloride accumulation in the leaves. A high level of potassium supply is frequently found to inhibit the uptake of calcium by plants (27), and the greater mobility of the potassium ion as compared with calcium is sometimes offered as an explanation. The sodium ion is, however, as mobile as the calcium.

This suggests that differential mobility between the sodium and calcium ions is irrelevant to the respective rates at which the ions are absorbed.

In the Na_2SO_4 series, increasing amounts of salt in the solution had no effect on the concentration of Ca^{++} in the stems and roots, but resulted in a marked progressive decrease in the Ca^{++} concentration of the leaves.

It is evident from table 2 that at comparable osmotic levels the plants in the NaCl series absorbed a considerably higher quantity of calcium than did the respective plants in the Na_2SO_4 series. Because of the low solubility product of CaSO_4 it might be assumed that the high concentrations of SO_4^{--} were lowering the solubility of the calcium added in the base nutrient solution. In

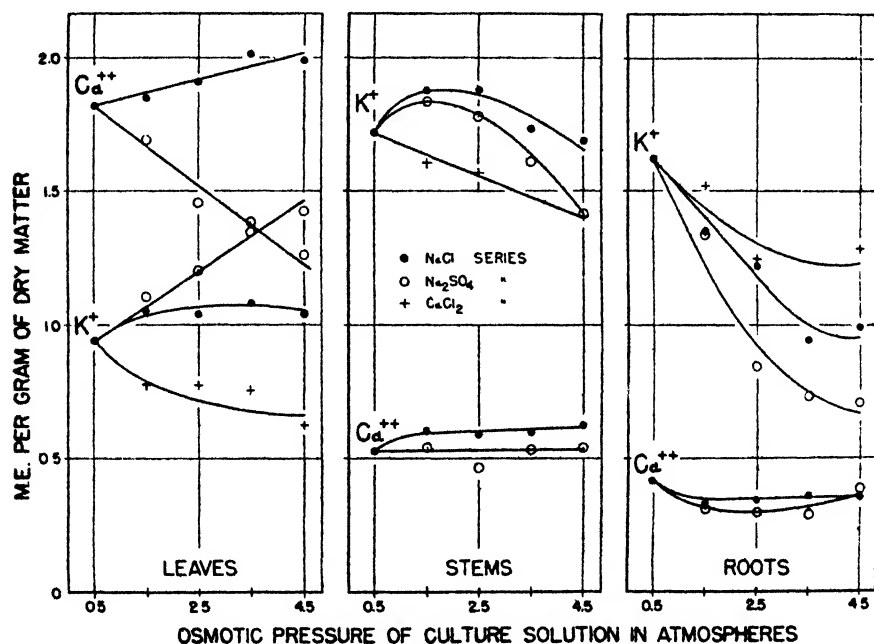


FIG. 5. EFFECT OF INCREASING AMOUNTS OF NaCl , CaCl_2 AND Na_2SO_4 ON THE UPTAKE OF IONS CONSTANT IN CONCENTRATION FOR ALL CULTURES

the highest concentration of Na_2SO_4 studied, however, CaSO_4 is soluble to the extent of 21 m.e./liter (31), whereas a maximum of only 5.9 m.e. of Ca per liter was present in the control culture solution. It is evident from this table that at isosmotic levels the Na_2SO_4 plants took up considerably more Na^+ than did those of the NaCl series—just the reverse situation observed with respect to calcium. Apparently the higher density of negative charge on the SO_4^{--} had its postulated effect (28, 29) in increasing membrane permeability to the monovalent Na^+ , but this effect did not hold with respect to membrane permeability for the divalent Ca^{++} .

Potassium. There were marked differences in the concentration of K^+ in the leaves, stems, and roots, as affected by the addition of these different salts

to the base nutrient solution (fig. 5). Apparently the concentration of K^+ in the roots was conditioned by two factors: (a) the osmotic pressure of the solution (for the roots of plants in saline cultures had lower concentrations of K^+ than the roots of the controls), and (b) the kind of salt present in excess. The trends of the curves showing K^+ concentration in the roots of each of the three series are so nearly the reverse of those for concentration of Na^+ or Ca^{++} in roots of respective series (fig. 4), that it would seem that the concentration of K^+ in this tissue is conditioned largely by the accumulation of the *other* cations in the roots. Thus more Na^+ was found in roots of the Na_2SO_4 series than in those of the $NaCl$ plants, and the content of K^+ was just the reverse.

It is difficult to offer a satisfactory explanation as to why the highest level of K^+ found in the roots of the $CaCl_2$ plants is associated with the lowest level found in the leaves, and *vice versa* for the Na_2SO_4 series. To say that a high concentration of K^+ in the roots is correlated with a low concentration in the leaves is merely a restatement of an observation, and in no way suffices for or offers an explanation. Moreover, it is the direct opposite of what might be anticipated.

There is an inverse relationship between the concentrations of Ca^{++} and K^+ in the leaves (figs. 4 and 5). Lindner and Harley (20), working with the problem of "lime-induced" chlorosis of pears and apples, noted that the severity of the symptoms were associated with shifts in the K/Ca balance. Soil conditions conducive to marked increases in the K^+ content of the leaves induced a lowering of the Ca^{++} content. This situation is frequently observed (27).

Phosphate. There was very little effect of either the type of added salt or the addition of various amounts of these salts on the concentration of phosphate in the different parts of the plant. In the $CaCl_2$ series the concentration of phosphate in the leaves decreased progressively with serial increases in the amount of $CaCl_2$ in the solution. The concentrations of phosphate in the roots of the Na_2SO_4 series showed no consistent trends, and it may be that many of the variations observed were fortuitous. Earlier work with barley (9) in which in one case 100 m.e. of chloride per liter and in another 200 m.e./liter of sulfate salts as mixed cations were added had no significant effect on the concentration of phosphate in the tops of 5-week-old plants. The roots were not analyzed. In an exhaustive study of the effect of the toxicity of chloride and sulfate salts (as mixed cations), Eaton (8) noted that "the concentrations [of phosphate] were not influenced to any major extent by the uptake of other ions."

Total nitrogen. Increasing concentrations of salt in the solution had relatively little effect on total nitrogen, but the general trend was toward a decrease. This finding is in contrast with the work of Hayward and Long (16) on tomato, of Gauch and Eaton (9) on barley, and of Wadleigh and Ayers (33) with bean plants grown in soil. In order to reconcile these contrasting results of earlier work with this present experiment, cognizance should be taken of the fact that these plants were grown during December when radiant energy is at a minimum for the year. As a consequence, the rate of carbohydrate synthesis was relatively low (32), and the status of carbohydrate reserves is known to have a marked effect upon nitrogen absorption and assimilation.

The concentration of total nitrogen in the leaves, stems, and roots of the bean plants grown with Na_2SO_4 as the added salt tended to be higher than with either of the other two salts. Loo (21) found that the sulfate ion tended to increase nitrate absorption.

SUMMARY

Red kidney bean plants were grown to the flowering stage in aerated solution culture with base nutrient solution, and in base nutrient solutions to which various amounts of CaCl_2 , of NaCl , and of Na_2SO_4 were added. These three salts were added individually to the base nutrient solution in quantities sufficient to raise the osmotic pressure by increments of 1, 2, 3, and 4 atmospheres. The addition of these salts to the base nutrient affected not only the concentration of the ions of the added salt in the plant, but in some cases the uptake of base nutrient ions, as follows:

Calcium. The addition of CaCl_2 to the solution resulted in an increase in the concentration of Ca^{++} in the leaves, stems, and roots, but the increase was by no means proportional to the amounts added. The most striking effect of the addition of either NaCl or Na_2SO_4 was the pronounced, progressive decrease in concentration of Ca^{++} in the leaves of the Na_2SO_4 plants as the amount of this salt in the solution was increased.

Sodium. When NaCl or Na_2SO_4 was added to the solution there was only a very slight increase over the low Na^+ concentration which prevailed in the leaves normally, but there was a moderate increase in the concentration of Na^+ in the stems. There was, however, a striking increase in the content of Na^+ in the roots. At any given equivalent concentration of Na^+ , the plants contained higher percentages of Na^+ when subjected to Na_2SO_4 than when NaCl was the added salt.

The mechanism by which Na^+ accumulated to such a marked degree in the roots with so little change in the concentration in the tops is not known.

Chloride. The plants took up considerable quantities of chloride. In the roots there were higher concentrations of chloride when NaCl was the added salt rather than CaCl_2 .

Sulfate. The concentration of sulfate in the roots was very closely paralleled by a similar increase in the leaves. The first increment of Na_2SO_4 , however, brought about virtually no increase in the concentration of sulfate in any part of the plant, showing that the plants possessed the ability to "exclude" sulfate to a rather marked degree as compared with chloride.

Potassium. Concentrations of K^+ in the leaves were inversely related to the trends for Ca^{++} concentrations in the leaves in the CaCl_2 series. NaCl in the substrate had little effect on either Ca^{++} or K^+ in the leaves. The addition of Na_2SO_4 to the solution resulted in a marked progressive lowering of the Ca^{++} content in the leaves, and a corresponding increase in K^+ concentration. In the roots, the higher concentrations of K^+ were associated with the lower concentrations of other cations (CaCl_2 series); and the lower concentrations of K^+ in the roots were associated with the higher content of other cations (Na_2SO_4 series).

Phosphate. The addition of salt to the base nutrient solution, regardless of the types of salt or concentrations employed, had very little effect on phosphate concentrations in the plant parts.

Total nitrogen. Increasing amounts of the three salts tended to decrease progressively the concentration of total nitrogen in the plant tissues, but this effect was attributed to season of the year. The values were appreciably higher in the Na_2SO_4 series than in the other two series of plants.

The data reported herein tend to corroborate the evidence that salt absorption involves an extremely complex series of interrelated processes.

REFERENCES

- (1) ASSOCIATION OFFICIAL AGRICULTURAL CHEMISTS 1940 Official and Tentative Methods of Analysis, ed. 5. Washington, D. C.
- (2) BROADFOOT, W. M., AND BROWNING, G. M. 1941 Factors influencing determination of sodium in plant material. *Jour. Assoc. Off. Agr. Chem.* 24: 916-926.
- (3) CHAMBERS, R., AND REZNIKOFF, P. 1925 The reaction of the protoplasm of the living amoeba to injected salts. *Proc. Soc. Exp. Biol. and Med.* 22: 320-322.
- (4) CHIBNALL, A., AND CHANNON, H. 1929 The ether-soluble substances of cabbage leaf cytoplasm: VI. Summary and general conclusions. *Biochem. Jour.* 23: 176-184.
- (5) COLLANDER, R. 1941 Selective absorption of cations by higher plants. *Plant Physiol.* 16: 691-720.
- (6) EATON, F. M. 1941 Plant culture equipment. *Plant Physiol.* 16: 385-392.
- (7) EATON, F. M. 1941 Water uptake and root growth as influenced by inequalities in the concentration of the substrate. *Plant Physiol.* 16: 545-564.
- (8) EATON, F. M. 1942 Toxicity and accumulation of chloride and sulfate salts in plants. *Jour. Agr. Res.* 64: 357-399.
- (9) GAUCH, H. G., AND EATON, F. M. 1942 Effect of saline substrates on hourly levels of carbohydrates and inorganic constituents of barley plants. *Plant Physiol.* 17: 347-365.
- (10) GAUCH, H. G., AND MAGISTAD, O. C. 1943 Growth of strawberry clover varieties and of alfalfa and Ladino clover as affected by salt. *Jour. Amer. Soc. Agron.* 35: 871-880.
- (11) GAUCH, H. G., AND WADLEIGH, C. H. 1944 The influence of high salt concentrations on the growth of bean plants. *Bot. Gaz.* 105: 379-387.
- (12) HARRIS, J. A., *et al.* 1924 The tissue fluids of Egyptian and upland cottons and their F_1 hybrid. *Jour. Agr. Res.* 27: 267-327.
- (13) HARRIS, J. A., HOFFMAN, W. F., AND LAWRENCE, J. V. 1925 Differential absorption of anions by varieties of cotton. *Proc. Soc. Exp. Biol. and Med.* 22: 350-352.
- (14) HAYWARD, H. E., AND LONG, E. M. 1941 Anatomical and physiological responses of the tomato to varying concentrations of sodium chloride, sodium sulphate, and nutrient solutions. *Bot. Gaz.* 102: 437-462.
- (15) HAYWARD, H. E., AND LONG, E. M. 1942 Vegetative responses of the Elberta peach on Lovell and Shalil rootstocks to high chloride and sulfate solutions. *Proc. Amer. Soc. Hort. Sci.* 41: 149-155.
- (16) HAYWARD, H. E., AND LONG, E. M. 1943 Some effects of sodium salts on the growth of the tomato. *Plant Physiol.* 18: 556-569.
- (17) HAYWARD, H. E., AND SPURR, W. B. 1944 The tolerance of flax to saline conditions. Effect of sodium chloride, calcium chloride, and sodium sulfate. *Jour. Amer. Soc. Agron.* 36: 287-300.
- (18) HEILBRUNN, L. V., AND DAUGHERTY, K. 1932 The action of sodium, potassium, calcium, and magnesium ions on the plasmogel of *Amoeba proteus*. *Physiol. Zool.* 5: 254-274.
- (19) LEEB, J. J. 1942 The importance of sodium for plant nutrition: III. The equilibrium of cations in the beet. *Soil Sci.* 53: 399-411.
- (20) LINDNER, R. C., AND HARLEY, C. P. 1944 Nutrient interrelations in lime-induced chlorosis. *Plant Physiol.* 19: 420-439.
- (21) LOO, T. 1931 Further studies on the absorption of ammonia and nitrate by the root systems of the higher plants. [In English.] *Sun Yatsen Univ. Col. Sci. Dept. Biol. Bul.* 10: 1-130.
- (22) MAGISTAD, O. C., ET AL. 1943 The effect of salt concentration, kind of salt, and climate on plant growth in sand cultures. *Plant Physiol.* 18: 151-166.
- (23) MAGISTAD, O. C., AND REITEMEIER, R. F. 1943 Soil solution concentrations at the wilting point and their correlation with plant growth. *Soil Sci.* 55: 351-360.

- (24) MOYER, L. S., AND BULL, H. B. 1935 Electrokinetics: XVII. Surface charge and ion antagonism. *Jour. Gen. Physiol.* 19: 239-247.
- (25) NATIONAL RESOURCES PLANNING BOARD 1942 The Pecos River Joint Investigation. Reports of the participating agencies. U. S. Government Printing Office, Washington, D. C.
- (26) OSTERHOUT, W. J. V. 1943 A model of the potassium effect. *Jour. Gen. Physiol.* 27: 91-100.
- (27) PIERRE, W. H., AND BOWER, C. A. 1943 Potassium absorption by plants as affected by cationic relationships. *Soil Sci.* 55: 23-36.
- (28) RABER, O. 1923 Permeability of the cell to electrolytes. *Bot. Gaz.* 75: 298-308.
- (29) RABER, O. 1926 Electrostatic theory of permeability. *Bot. Gaz.* 81: 348-352.
- (30) RANKER, E. R. 1927 A modification of the salicyliethiosulfate methods suitable for the determination of total N in plants, plant solutions, and soil extracts. *Jour. Assoc. Off. Agr. Chem.* 10: 230-251.
- (31) SEIDELL, A. 1940 Solubilities of Inorganic and Metal Organic Compounds, vol. 1, ed. 3. D. van Nostrand Co., Inc., New York, N. Y.
- (32) WADLEIGH, C. H., AND GAUCH, H. G. 1942 Assimilation in bean plants of nitrogen from saline solutions. *Proc. Amer. Soc. Hort. Sci.* 41: 360-364.
- (33) WADLEIGH, C. H., AND AYERS, A. D. Influence of salt concentration and soil moisture content upon the biochemical composition of bean plants. *Plant Physiol.* (In press).

THE DIVERGENT BEHAVIOR OF KPO_3 AND K_2SO_4 IN SOILS, WITH AND WITHOUT LIMESTONE AND DOLOMITE

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Potassium metaphosphate affords a combination of two fertilizer elements in high concentration, with attendant economy in transportation and handling. In texts, the formula of the reagent salt is given as $K_4(PO_3)_4 \cdot 2H_2O$ (3, p. 432) and as $2KPO_3 \cdot 3H_2O$ (12, pp. 981-985) and is listed as "slightly soluble" in water. The K-metaphosphate used in the presently reported studies, however,

was a "white crystalline" anhydrous product, $\begin{array}{c} O \\ \parallel \\ P-OK \\ \parallel \\ O \end{array}$, that gave a 3 per cent

aqueous solution at 30° C. It was made by blowing muriate of potash into a reaction chamber containing the fumes of burned phosphorus at high temperature (1, 2). In the conventional terminology of fertilizer analyses, the components are expressed as percentages of K_2O and P_2O_5 per 2 mols of KPO_3 , or $K_2P_2O_6$. In unpublished pot culture findings, the response to the anhydrous K-metaphosphate that carried 51.6 per cent P_2O_5 and 34.9 per cent K_2O was virtually identical with the response to an equivalent mixture of K_2SO_4 and superphosphate. Since previous studies had indicated that PO_3 and PO_4 behave alike, when incorporated in the respective forms of $Ca(PO_3)_2$ and $CaH_4(PO_4)_2$ (6), the present postulation is that PO_3 of the K-metaphosphate undergoes conversion to PO_4 and functions as such in the soil.

OBJECTIVE

The present objective is to record compositions of leachings that reflect the distinctive behavior of incorporations of K-metaphosphate in two important soils, alone and with limestone and with dolomite, as reflected by rain-water leachings during the initial year of an outdoor lysimeter experiment, in which recoveries of K from equivalent quantities of KPO_3 and K_2SO_4 were integrated with outgo of Ca, Mg, and SO_4 .

EXPERIMENTAL

The soils used were Hartsells fine sandy loam and Fullerton silt loam, described in recent contributions (9, 10, 11). It is emphasized that the potassic compounds were incorporated, in contradistinction to the surface applications in related experiments (5, 7, 8, 9). The two soils were limed to full depth at respective rates of 5,000 and 2,775 pounds of $CaCO_3$ -equivalence per 2,000,000 pounds of soil. These 100-mesh incorporations were allowed to undergo disintegration prior to the incorporation of the two carriers of K. The pH of the Hartsells soil was 4.8 initially and 4.6 after 21 months of exposure,

whereas the Fullerton soil registered pH values of 5.0 and 4.9 for corresponding determinations. Twenty-one months after the incorporations of KPO_3 to supply K_2O at the 1,000-pound rate, the Hartsells and Fullerton soils showed respective pH values of 4.9 and 5.3.

The rain-water leachings from a 57.52-inch precipitation passed directly from the treated soils and into the leachate receptacles, and hence the composition of the leachings was not subjected to the vitiative effect of a stratum of subsoil. Although the K content of every periodic collection of leachates was determined, the results are condensed to expressions of annual outgo in table 1. The quantities of Ca and Mg leached are expressed jointly in terms of $CaCO_3$, along with the annual outgo of sulfates. The $CaCO_3$ -equivalence of every Mg outgo is shown, however, in juxtaposition to its inclusion in Ca + Mg outgo, to facilitate consideration of the differential effects of the two potassic compounds upon the proportions of Ca and Mg in the respective leachings from limestone and dolomite.

Hartsells soil

Outgo of K. The recovery of potassium from the unlimed soil that received the 200-pound incorporation of K_2O as KPO_3 amounted to 39 per cent of the input, as against a 50 per cent recovery from K_2SO_4 , whereas the corresponding recoveries from the heavier incorporations were 41 per cent and 30 per cent for the phosphate and the sulfate, respectively. The recovery of potassium from every 1,000-pound K_2O incorporation exceeded that from the corresponding incorporation at the 200-pound rate.

Every incorporation of limestone and of dolomite induced a substantial repression in the outgo of potassium, in consonance with previous findings (4). This repression was exerted upon the outgo of K from the supply native to the soil and also upon the outgo from every input of K as either phosphate or sulfate. The most marked repressive effect was that induced by the limestone upon the outgo of K from the K_2SO_4 incorporation that supplied K_2O at the 1,000-pound rate.

Outgo of Ca + Mg. The two types of limestone induced identical 2.5-fold increases in the outgo of Ca + Mg from the soil that received no K. Companion incorporations of KPO_3 at the 200-pound K_2O rate did not alter these increases appreciably, whereas the outgo from the limestone was increased by the corresponding incorporation of K_2SO_4 . The 1,000-pound K_2O incorporation of KPO_3 repressed slightly the outgo of Ca + Mg from dolomite, one fourth of the repression being accounted for by Ca and three fourths by Mg. At the 1,000-pound K_2O rate, the repression induced by KPO_3 amounted to a fourth of the outgo of Ca from the limestone alone. In contrast, the heavy incorporation of K_2SO_4 induced the maximal outgo of Ca + Mg from the limestoned soil, and the increase in outgo was accounted for solely by enhancement in the leaching of Ca.

Apparently, the added metaphosphate underwent hydration while in the form of KPO_3 or after an equivalence of $Ca(PO_3)_2$ was formed in the soil. In either instance, the ultimate effect was the deposition of basic orthophosphates of calcium, and the concomitant fixation of K effected no release of Ca and Mg

TABLE 1

Divergence in behavior of potassium incorporated as K-metaphosphate and as K_2SO_4 in two soils, with and without limestone and dolomite, as shown by variance in outgo of K, Ca, Mg, and sulfates

OUTGO, POUNDS PER 2,000,000 POUNDS OF SOIL										
LIME MATERIAL*	Hartsells fine sandy loam					Fullerton silt loam				
	No K added	From additions of K ₂ O				No K added	From additions of K ₂ O			
		200 pounds		1000 pounds			200 pounds		1000 pounds	
		As KPO ₃	As K ₂ SO ₄	As KPO ₃	As K ₂ SO ₄		As KPO ₃	As K ₂ SO ₄	As KPO ₃	As K ₂ SO ₄
		<i>K₂O</i>								
None.....	19	96	118	426	321	55	114	147	345	264
Limestone.....	5	23	29	295	134	30	87	98	407	240
Dolomite.....	6	25		348	...	31	83	...	380	...
<i>Ca + Mg, as CaCO₃</i>										
None.....	354 ⁽⁷⁸⁾ †	269 ⁽⁶⁸⁾	315 ⁽⁸⁹⁾	209 ⁽⁶⁸⁾	433 ⁽¹¹⁰⁾	510 ⁽¹⁰⁰⁾	352 ⁽⁷²⁾	455 ⁽⁹²⁾	189 ⁽⁴⁷⁾	405 ⁽⁸⁰⁾
Limestone.....	1216 ⁽⁹⁸⁾	1193 ⁽⁹²⁾	1423 ⁽⁶¹⁾	955 ⁽⁶³⁾	1512 ⁽⁹⁹⁾	848 ⁽⁸⁷⁾	649 ⁽⁷²⁾	838 ⁽⁹⁰⁾	441 ⁽⁸⁶⁾	881 ⁽⁹⁰⁾
Dolomite.....	1212 ⁽⁹⁴⁾	1251 ⁽⁶⁰⁰⁾	...	1165 ⁽⁶⁰⁷⁾	...	919 ⁽⁶⁰⁸⁾	566 ⁽³²⁷⁾	...	424 ⁽²⁰⁰⁾
<i>SO₃</i>										
None.....	55	94	181	190	405	75	75	184	105	318
Limestone.....	229	228	381	242	594	170	135	285	162	500
Dolomite.....	224	246	...	269	...	184	136	...	163	...

* At per acre rate of 5,000 pounds and 2,775 pounds of $CaCO_3$ for Hartsells and Fullerton soils, respectively; full-depth incorporation.

† The figures in brackets show the $CaCO_3$ -equivalence accounted for by magnesium content.

(13). The effect would parallel that induced by the incorporation of an alkaline potassic phosphate, in contrast to the exchange activity of the neutral K_2SO_4 , which induced an increase in solute Ca. From the foregoing, it is obvious that although K_2SO_4 induced a substantial exchange of K for Ca in the Hartsells soil, unlimed and limed, as in previous experiments with topdressings (5, 7, 9), the effect of KPO_3 was to conserve the Ca and Mg of both native and additive supplies.

Outgo of sulfates. The outgo of sulfates from the 200-pound incorporation of K_2O as KPO_3 was virtually twice the outgo from the unlimed soil. At the 1,000-pound K_2O rate, KPO_3 induced a still greater sulfate outgo, one that exceeded the outgo from the 200-pound K_2O incorporation as K_2SO_4 . As usual, the early effect of limestone and of dolomite was to accelerate sulfate leachings. Hence, when KPO_3 was incorporated at the 200-pound K_2O rate with the liming materials, its accelerative influence upon sulfate outgo was either nullified or masked. In its joint incorporations with limestone and dolomite at the 1,000-pound K_2O rate, however, KPO_3 accelerated the sulfate outgo while repressing the outgo of Ca + Mg. This may mean that the recovery of K from that added as KPO_3 is due to outgo of K_2SO_4 .

The foregoing results indicate that sulfate outgo was affected alike by single incorporations of K-metaphosphate, limestone, and dolomite. The K-metaphosphate either promoted sulfonation or altered the propensity of the soil to retain sulfates. Both of these effects are induced, however, by incorporations of limestone and dolomite with the Hartsells soil. Unlimed, it exhibits a marked tendency to retain additive sulfates and releases them when limed or dolomited (7, 8, 9). The increase in sulfate outgo from the KPO_3 incorporations may be due, therefore, to a combination of the two factors—increased generation of sulfates and increase in their leachability.

Fullerton soil

Outgo of K. The recoveries of K from the incorporations of KPO_3 and K_2SO_4 with the unlimed soil were 30 per cent and 46 per cent, respectively, and the greater retention of the K supplied by KPO_3 is in harmony with the findings for the Hartsells soil. Again, however, the recovery of K from KPO_3 at the 1,000-pound K_2O rate exceeded substantially the recovery from the equivalent incorporation of K_2SO_4 . The repressive effect of limestone and of dolomite upon the outgo of K from the larger stores of exchangeable K in the Fullerton soil was greater in extent, although proportionately less, than the corresponding repression in the outgo of K from stores native to the Hartsells soil.

Both limestone and dolomite caused a marked repression in the outgo of K from the 200-pound K_2O incorporation of both metaphosphate and sulfate, and the high-calcic limestone acted likewise upon the outgo of K from the heavy incorporation of K_2SO_4 . The reverse effect was registered by limestone and by dolomite, however, upon the outgo of K from the 1,000-pound K_2O incorporation as KPO_3 .

Outgo of Ca + Mg. The metaphosphate and the liming materials again were

reciprocal in their repressive effects upon the leachings of Ca + Mg and K. The 510-pound outgo of Ca + Mg from the unlimed soil was decreased a third by the 200-pound incorporation of K_2O as KPO_3 and 63 per cent by the 1,000-pound incorporation. A like repression was induced when KPO_3 was incorporated jointly with limestone and with dolomite. The maximal repression was the 495-pound difference between the Ca + Mg outgo from dolomite alone and the corresponding outgo from dolomite plus the heavier incorporation of KPO_3 . Obviously, this diminution in the concentration of solute Ca + Mg in the leachates is attributable to combination between these bases and the ultimate PO_4 derivative from the added K-metaphosphate.

In this silt loam of higher content of exchangeable Ca, Mg, and K, the two K_2SO_4 incorporations exerted little effect upon the outgo of Ca + Mg from native supplies or from those supplied by limestone.

Sulfate outgo. The outgo of sulfates from the unlimed Fullerton soil was not increased by the 200-pound K_2O incorporation as KPO_3 , although it was increased significantly by the heavy incorporation. Increases in sulfate outgo were induced singly by limestone and dolomite, but the increases were not enhanced or even equalled by joint incorporation of the liming materials with KPO_3 at either rate. Since the outgo of sulfates derived from the incorporated K_2SO_4 was accelerated by limestone, it follows that similar acceleration would have been exerted upon an augmented supply of sulfates, had these been generated through the stimulative influence of KPO_3 in association with limestone. Apparently, therefore, the several degrees to which sulfate generation was increased by sole additions of KPO_3 were not furthered by the supplemental liming materials, which, of themselves, are conducive to increase in both sulfication and sulfate leachability (7, 8, 9).

Expressed in relation to the overall influence of the liming materials upon sulfate formation and leachability, maximal effect appears to have been induced by limestone and by dolomite without KPO_3 , whereas leachability of sulfates derived from K_2SO_4 was increased to a marked extent by limestone. Although dolomite was not incorporated jointly with K_2SO_4 in the present study, a like effect can be attributed to it upon the basis of previous findings which demonstrated that incorporations of dolomite are even more accelerative than limestone upon the outgo of additive sulfates (8).

DISCUSSION

The leachate compositions demonstrate that recovery of K from KPO_3 is less than that from K_2SO_4 at the 200-pound K_2O rate on both soils, unlimed, limed, and dolomited. When the phosphate and sulfate were incorporated at the 1,000-pound K_2O rate, however, the recovery of K from KPO_3 was invariably the greater. In one respect, the fate of K added as the metaphosphate was similar to the fate of K added as K_2SO_4 . The outgo of K from incorporations of both KPO_3 and K_2SO_4 at the two rates was repressed by both liming materials in the Hartsells soil of low exchangeable Ca and Mg content. The outgo of K from the 200-pound K_2O incorporations of both of the potassic salts was also re-

pressed by limestone in the Fullerton soil of higher content of exchangeable Ca + Mg. This repressive effect of limestone in the Fullerton soil was registered also by the diminution in outgo of K from K_2SO_4 at the 1,000-pound K_2O rate. In contrast, limestone and dolomite accelerated somewhat the outgo of K from the corresponding heavy incorporation of KPO_3 , a concomitant effect being a marked decrease in the outgo of Ca + Mg from the two liming materials.

It is evident that the effect of K-metaphosphate upon outgo of calcium, and of magnesium, is opposite to the expectancy from conventional potassium salts. The K-metaphosphate induced substantial repressions in the outgo of Ca and Mg, whereas muriate, nitrate, and sulfate of potassium usually induce increases in such outgo (9). With increase in rate of KPO_3 incorporation, the repression upon outgo of Ca + Mg was furthered. The repression may be due in part to progressive precipitations of Ca + Mg that would have been in the leachates had there been no soluble phosphates in the soil. Nevertheless, the recoveries of K from the heavy incorporations of KPO_3 indicate that the entrance of K into the soil complex has resulted in a diminution in the outgo of neutral salts of Ca and Mg. This conservation of Ca + Mg is exerted upon both native supplies and increments from the limestone and dolomite. The postulation as to transition of PO_3 to PO_4 and attendant effect upon outgo of Ca + Mg is supported by related unpublished findings from incorporations of monocalcium phosphate and H_3PO_4 .

The leachate compositions gave no indications as to exchange between the K of KPO_3 and the Ca and Mg of the soil. If such exchange did occur it was masked by the precipitative effect of the added PO_3 upon any K-liberated Ca and Mg. Although the light incorporations of K_2SO_4 induced the anticipated depletion of soil content of Ca and Mg, a large fraction of the K_2SO_4 was leached unchanged, as was true in comparisons with KCl and KNO_3 (9). In absence of evidence of exchange between the K of KPO_3 and the Ca + Mg of the soil, it is indicated that the marked conservation of these two elements by the incorporations of K-metaphosphate was due in part to the protective action of the additive K in the soil complex.

When outgo of calcium and magnesium is expressed jointly in terms of $CaCO_3$, it is not apparent to what extent the two types of limestone affect the proportions of Ca and Mg in the leachates. The reported enhancements in outgo of Ca + Mg from the limestone were accounted for solely by calcium. Invariably, the magnesium content of the leachates from the limed soil was less than the magnesium outgo from the unlimed soil. That effect was induced also by KPO_3 in the unlimed soil, whereas K_2SO_4 effected releases of Mg to the leachings. When limestone and KPO_3 were incorporated jointly, the two materials functioned alike in bringing magnesium content of the limestone leachates to a level below the magnesium content of leachates from the untreated soil; but, when limestone and K_2SO_4 were incorporated jointly, the limestone nullified the tendency of the added K to liberate Mg.

The increase in outgo of Ca + Mg from dolomite alone was accounted for by 2 to 1 and 3 to 1 proportions of magnesium to calcium from the Hartsells and Fullerton soils, respectively. At the 200-pound K_2O rate, the incorporation of

KPO₃ with dolomite brought no appreciable variance in outgo of Ca + Mg from the Hartsells soil, or in the ratio of the bases in the leachates. At the 1,000-pound K₂O rate, however, the KPO₃ repressed the outgo of both Ca and Mg from dolomite to quantities one-half those from the dolomite alone. The ratio of Mg to Ca in the enhanced outgo of Ca + Mg, therefore, was virtually the same in the leachates from dolomite alone and from dolomite with the heavy and lighter additions of KPO₃. In the Fullerton soil of higher content of exchangeable Ca and Mg, however, the incorporation of KPO₃ at both rates caused marked diminutions in the outgo of both Ca and Mg, the effect of the larger incorporation being the more pronounced.

In several previous lysimeter studies it was observed that the increase in Ca + Mg outgo from dolomite, after its disintegration, was accounted for chiefly and even solely by enhancement in outgo of magnesium. Quite frequently, the outgo of Ca from rational incorporations of dolomite has been significantly less than the outgo of Ca from the untreated soil. In all of the leachates of dolomite in table 1, however, enhancement in outgo of Ca + Mg from dolomite was accounted for in part by Ca. With the single exception of the joint incorporation of dolomite with KPO₃ at the 1,000-pound K₂O rate in the Fullerton soil, dolomite imparted a marked preponderance of Mg to the leachates. In this exception, wherein the Ca + Mg outgo was 495 pounds less than the outgo of Ca + Mg from dolomite alone, the 286-pound repression in outgo of Ca was offset by only a 100-pound increase in outgo of Mg. The function of the KPO₃ apparently was to cause major precipitations of calcic phosphates and minor precipitations of magnesium phosphates in the limestoned soils and substantial precipitations of both calcic and magnesian phosphate in the dolomited soils.

SUMMARY

Distinctive differences in the behavior of full-depth incorporations of a "semi-works" K-metaphosphate and K₂SO₄ were established by lysimeter leachings from two soils, with and without limestone and dolomite.

During the initial year, the retention of K from every light incorporation of KPO₃ exceeded that from its corresponding incorporation of K₂SO₄; at the heavy rate, the reverse was true for unlimed and limestoned soils.

Limestone and dolomite repressed the outgo of K from native stores and from every potassic addition save the heavy incorporation of KPO₃ with the silt loam of higher exchangeable K-Ca-Mg content.

K-metaphosphate diminished the outgo of Ca and Mg from their native stores in both soils and from the quantities supplied by limestone and dolomite.

Magnesium outgo was repressed by every limestone incorporation, alone and with either K₂SO₄ or KPO₃.

Enhancements in outgo of Ca + Mg from dolomite alone were due to Mg:Ca proportions as high as 3 to 1. In the lessened outgo of both Ca and Mg from dolomite in its joint addition with KPO₃, the two bases were leached in more equal proportion.

The reciprocal effects induced by KPO₃, limestone, and dolomite upon outgo of K, Ca, and Mg are attributable to different mechanisms. The conservation

of Ca and Mg induced by K-metaphosphate, in contrast to the exchange and consequential depletion induced by K_2SO_4 , is attributed to phosphate precipitations of the two bases that otherwise would have been retained in the leachates, and to protective action of the K of KPO_3 upon the Ca and Mg in the soil complex. The concomitant fixation of the K from the light addition of the readily soluble KPO_3 occurred as though the K were added in alkaline form. Because of the greater precipitation of Ca and Mg induced by KPO_3 at the heavy rate, accompanied by enhancement in sulfate outgo and lessened retention of the incorporated K, the resultant recovery of K can be attributed to outgo of K_2SO_4 .

Incorporated alone, K-metaphosphate apparently stimulated sulfocification, as indicated by marked increase in sulfate outgo from both soils; incorporated with limestone, and with dolomite, it did not augment the corresponding accelerative effect of the two liming materials. Leachability of sulfates derived from K_2SO_4 was increased by the disintegrated incorporations of limestone.

REFERENCES

- (1) COPSON, R. L., POLE, G. R., AND BASKERVILL, W. H. 1942 Development of processes for metaphosphate production. *Indus. and Engin. Chem., Indus. Ed.* 34: 26-32.
- (2) CURTIS, H. A., COPSON, R. L., AND ABRAMS, A. J. 1937 Metaphosphate investigations. *Chem. and Metall. Engin.* 44: 140-142.
- (3) HODGMAN, C. D. (Editor) 1937 Handbook of Chemistry and Physics, ed. 21. Chemical Rubber Publishing Company, Cleveland, Ohio.
- (4) MACINTIRE, W. H., SHAW, W. M., AND YOUNG, J. B. 1930 The repressive effect of lime and magnesia upon soil and subsoil potash. *Jour. Agr. Sci. [England]* 20: 499-510.
- (5) MACINTIRE, W. H., ET AL. 1936 The effects of 12 year residues of lime and magnesia upon the outgo of subsequent additions of potash. *Jour. Amer. Soc. Agron.* 28: 202-215.
- (6) MACINTIRE, W. H., HARDIN, L. J., AND OLDHAM, F. D. 1937 Calcium metaphosphate fertilizers: chemical composition and properties. *Indus. and Engin. Chem.* 29: 224-234.
- (7) MACINTIRE, W. H., ET AL. 1938 Behavior of calcium, magnesium, and potassium sulfates, as influenced by limestone and by dolomite—a lysimeter study. *Soil Sci.* 46: 229-247.
- (8) MACINTIRE, W. H., SHAW, W. M., AND ROBINSON, B. 1941 Influence of limestone and dolomite upon sulfate retention from annual additions of potassium sulfate. *Soil Sci.* 51: 73-84.
- (9) MACINTIRE, W. H., ET AL. 1943 Potassium retention from annual additions of chloride, sulfate, and nitrate, as influenced by limestone and dolomite. *Soil Sci.* 55: 321-332.
- (10) MACINTIRE, W. H., ET AL. 1944 Industrial precipitated tricalcium phosphates: variance in chemical, structural, and fertilizer properties. *Indus. and Engin. Chem.* 36: 550.
- (11) MACINTIRE, W. H., ET AL. 1944 Fused tricalcium phosphate: relation of degree of defluorination to fertilizer value of quenched fusions of rock phosphate. *Soil Sci.* 57: 425-442.
- (12) MELLOR, J. W. 1931 A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 8. Longmans, Green and Co., New York.
- (13) SHAW, W. M., AND MACINTIRE, W. H. 1937 The relationship between water-soluble, replaceable, and fixed fractions of potash additions to soils. *Soil Sci. Soc. Amer.* 1: 143-148.

MICROORGANISMS AND SOIL AGGREGATION: I. ORIGIN AND NATURE OF SOME OF THE AGGREGATING SUBSTANCES¹

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Organic residues when incorporated into the soil bring about increased aggregation of the soil particles (1, 2, 3, 7, 8, 19). In general, the more readily available an organic substance is to microbial attack, the greater its beneficial effect on soil granulation. More resistant materials are less effective and require longer periods of time for maximum aggregation to occur (8, 11).

When easily decomposable organic residues are added to the soil, aggregation quickly reaches a maximum, after which it tends to decrease slowly. Nevertheless, even after long periods of incubation considerable aggregation still persists (3, 8, 11). The initial high aggregation is brought about primarily by the numerous microbial cells and filaments which bind the soil particles together and by soil-aggregating substances synthesized or released from the organic materials by the activity of the soil population (7, 9, 10, 11, 12, 15, 18). The original organic residues may also contain small amounts of water-soluble aggregating substances (8). Some of these organic aggregating agents may be resistant to microbial decomposition, or they may unite both physically and chemically with the soil colloidal particles and the humus and thereby be rendered resistant to further change. On the other hand, as evidenced by the fact that aggregation does decrease, some of the initial soil-cementing substances are themselves destroyed or altered by other microbes until the remaining binding materials consist of more or less resistant complexes. During the decomposition process it is very probable that soil-aggregating substances are continually being produced and destroyed by the changing microbial population (7, 8, 9, 11).

From this brief review of investigations concerning the role of microorganisms and organic matter in the process of soil granulation, it is evident that the increased aggregation is brought about by one or more of the following:

- Cells and filaments of the numerous microorganisms that decompose the organic residues.
- Products of microbial synthesis.
- Decomposition products of microbial metabolism.
- Water-soluble aggregating substances contained in the original organic materials.

The study reported in this paper was undertaken in an attempt to determine the nature and relative effectiveness of some of the soil-aggregating agents resulting from microbial activity.

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EXPERIMENTAL

Methods

Two southern Idaho soils, Portneuf sandy loam collected from the vicinity of Twin Falls and Declo loam collected near Aberdeen,³ were used. Some physical and chemical properties of the two soils follow:

SOIL	pH	SAND	SILT	CLAY	MOISTURE- HOLDING CAPACITY*	NITROGEN†	ORGANIC MATTER‡
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Portneuf sandy loam . . .	8.0	66	24	10	43	0.090	0.95
Declo loam.....	8.0	46	41	13	40	0.118	1.46

* Hilgard cup method.

† Kjeldahl procedure.

‡ Digestion with chromic acid and titration with standard ferrous ammoniumsulfate

The effects of various treatments and substances on the aggregation of the silt and clay particles of the soils were determined by a pipette method similar to one used in previous studies (7). In this study, however, a mechanical pipette was used, and the degree of granulation is reported as the percentage by weight of the total silt and clay particles that are bound into water-stable aggregates larger than 50 μ in diameter. Before analysis all samples were dried at 50° C. and passed through a 3-mm. sieve.

Selection of cultures

In order to select cultures for further study various bacteria, actinomycetes, and fungi (see table 1) were isolated from the soil by the plate method. Two-hundred-gram portions of sterilized Portneuf sandy loam in 500-cc. Erlenmeyer flasks, to which 4 gm. of sucrose, 0.12 gm. of NaNO₃, and 0.1 gm. KH₂PO₄ had been added, were inoculated in duplicate with the cultures. The sucrose solution was sterilized separately and added aseptically to the flasks, sufficient moisture being included to bring the moisture content of the soil to 55 per cent of saturation. The flasks were incubated for 3 weeks at 25° C. and aggregate analyses run in duplicate on each soil portion.

The results, presented in table 1, show that the different microbes varied considerably in their binding effect. Only one organism, an antibiotic bacillus, produced no aggregation. The greatest influence (66 to 67 per cent aggregation) was exerted by an organism belonging to the *Bacillus subtilis*⁴ group and by the fungus *Cladosporium*. For this reason these two cultures were selected for further study.

³ These soils were selected and collected by H. W. E. Larson, extension specialist in soils, of the Idaho Station.

⁴ Inoculation of the bacillus into differential media indicated that the organism was related to the *Bacillus subtilis-mesentericus* group.

LIQUID CULTURE STUDIES

The *B. subtilis* sp. and the *Cladosporium* brought about marked aggregation when allowed to develop in the soil. The question immediately arose: Will these organisms when grown in liquid culture media produce substances which will aggregate the soil when they are incorporated with it, or is it necessary for them to grow and carry on their metabolic activities in the soil in order for ag-

TABLE 1

Effect of pure cultures of microorganisms on aggregation of silt and clay particles of Portneuf sandy loam*

Sucrose used as energy source

ORGANISM	UNAGGREGATED SILT + CLAY	AGGREGATION
	gm.†	per cent
Control.....	24.7	28
Control (soil + sugar + nutrients).....	24.5	28
<i>Bacillus subtilis</i> species.....	11.3	67
Chromogenic bacillus‡.....	18.2	47
Antibiotic bacillus.....	24.6	28
<i>Aerobacter aerogenes</i>	20.5	40
Soil actinomyces.....	18.8	45
<i>Aspergillus niger</i>	17.6	49
<i>Aspergillus</i> (yellow spores).....	19.4	44
<i>Rhizopus nigricans</i>	19.0	45
<i>Cladosporium</i>	11.6	66
<i>Alternaria</i>	16.4	52
<i>Penicillium</i>	16.5	52

* Soil contains 34.4 per cent total silt + clay.

† Per 100 gm. of soil.

‡ Aerobic bacillus producing bright yellow pigment.

gregation to occur? To elucidate this point the two microbes were cultured in the following synthetic medium:

Sucrose.....	20 gm.
KH_2PO_4	1.5 gm.
NaNO_3	2.0 gm.
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.5 gm.
KCl.....	0.3 gm.
Distilled water.....	1,000 ml.

pH adjusted to 6.5 to 7.0 with NaOH.

At 10-, 20-, 30-, and 40-day incubation periods (25° C.) 100-gm. portions of both the Declo and Portneuf soils were moistened to the saturation point with the liquid cultures. After drying at 50° C. the soil portions were moistened for the second time with the same material. In this manner the microbial products from approximately 2 gm. of sucrose were added to 100 gm. of soil. Both the

cells of the soil bacillus and substances produced by them were incorporated with the soil. In the case of the fungus, however, the pads were removed so that only the more or less soluble substances formed by the fungus were added. The soil portions were again dried at 50° C. and analyzed by the pipette method.

The *B. subtilis* sp. brought about even greater aggregation (table 2) than when it was allowed to develop in the soil. The fungus products, however, exerted only a moderate binding effect. With both organisms the concentration of soil-cementing materials was greatest after 10 days' incubation. Upon continued incubation these substances were either destroyed or altered so that the aggregating influence gradually decreased.

TABLE 2

Production of soil-aggregating substances in a liquid culture medium by Bacillus subtilis species and Cladosporium

Sucrose used as energy source

SOIL		PORTNEUF SANDY LOAM		DECLO LOAM	
Treatment		Unaggregated silt + clay	Aggregation	Unaggregated silt + clay	Aggregation
Organism	Incubation				
	days	gm.*	per cent†	gm.*	per cent†
Distilled water.....	00	25.8	25	40.6	25
Sterile medium.....	00	25.3	26	39.7	27
<i>Bacillus subtilis</i> sp.....	10	7.8	77	10.2	81
	20	8.9	74	16.1	70
	30	19.7	64
	40	21.7	60
	10	16.8	51	31.8	42
<i>Cladosporium</i>	20	22.9	33	34.1	37
	30	35.2	35
	40	37.5	31

* Per 100 gm. of soil.

† Aggregation of the silt and clay particles. The Portneuf soil contained 34.4 percent and the Declo soil 54.4 per cent total silt + clay.

It is apparent that a considerable part of the aggregating influence of the *Cladosporium* was due to the binding effect of the mycelial network which grew around the soil particles and held them tightly together. In the case of the soil bacillus both the cells and the substances produced by them were added to the soil. The resulting aggregation could have been brought about by the cells, by complexes produced by the cells, or by both. To obtain more specific information concerning this point, 10-day cultures of the bacillus were centrifuged in order to separate the cells from the rest of the medium. The supernatant liquid was removed and added to the soil in the usual manner. The cells were resuspended in water, again centrifuged, suspended in water a second time, and added to the soil. The state of aggregation of the silt and clay soil particles was then determined. The results, which were replicated many times, are recorded in table 3.

The aggregating effect of the soil bacillus was due to the combined effect of the cells and substances synthesized by the cells. By far the greater portion, however, was brought about by a substance or substances produced by the cells. The active material was found to be colloidal in nature. When freed from most of the residual sugar and soluble salts by dialyzing in parchment paper tubing for 48 hours, its aggregating influence increased. The addition of small amounts of sucrose decreased its effectiveness (table 3).

TABLE 3

*Effect of Bacillus subtilis sp. cells and substances produced by the cells on the aggregation of silt and clay soil particles**

SOIL	PORTNEUF SANDY LOAM		DECLLO LOAM	
	Unaggregated silt + clay	Aggregation	Unaggregated silt + clay	Aggregation
	gm.	per cent	gm.	per cent
Distilled water.....	25.6	26	40.4	26
Sterile medium....	25.5	26	39.8	27
Inoculated medium†.....	9.2	73	11.7	78
Medium minus cells‡ ...	15.1	56	23.1	58
Cells alone.....	22.2	35	35.1	36
Medium minus cell (dialyzed for 48 hours) ..	11.8	66	18.0	67
Same + 0.4 gm. sucrose	25.1	54

* Cells or substances produced by cells or both from 2 gm. of sucrose were added to 100 gm. of soil.

† Incubated for 10 days.

‡ Cells removed by centrifuging.

EFFECT OF NITROGEN AND ENERGY SOURCE

The influence of various nitrogen and energy sources on the production of aggregating substances by the soil bacillus was next investigated. For the study various nitrogen compounds (table 4) were substituted for the NaNO_3 and several sugars (table 5) for the sucrose of the base medium used in the previous experiments.

The results (table 4) of the nitrogen series show clearly that both inorganic and organic nitrogen sources are equally effective. The presence of asparagine, casein, and NaNO_3 resulted in the greatest aggregating influence. Urea, beef extract, and peptone were slightly less effective. When $(\text{NH}_4)_2\text{SO}_4$ was used the organisms grew very slowly. However, after 40 days' incubation a binding effect comparable to that of the urea medium after 20 days' incubation resulted. The most rapid production of cementing material occurred in the asparagine medium. With the exception of the casein and peptone, the sterile media had little influence on the soil structure. In the former cases, however, a moderate aggregating effect was produced, indicating that unaltered casein and peptone bring about increased soil granulation.

The influence of the energy source on the production of aggregating substances by the *B. subtilis* sp. was studied, asparagine being used in place of NaNO_3 in

the base medium. The results are recorded in table 5. The bacillus produced aggregating substances from dextrose, maltose, xylose, arabinose, and sucrose. The greatest binding occurred, however, with the sucrose medium. It was interesting to note that the dextrose medium after 20 days' incubation was thick and sirupy whereas the sucrose medium remained more or less watery. Despite

TABLE 4

*Effect of nitrogen source on the production of soil-aggregating substances from sucrose by a Bacillus subtilis species**

INCUBATION. days	STERILE MEDIUM 0		10		20	
	Unaggre- gated silt + clay	Aggre- gation	Unaggre- gated silt + clay	Aggre- gation	Unaggre- gated silt + clay	Aggre- gation
	gm.†	per cent	gm.†	per cent	gm.†	per cent
Check—distilled water	40.9	25	40.3	26	40.7	25
NaNO ₃	38.6	29	17.6	68	12.9	76
Urea.....	38.6	29	19.8	64	23.1	58
Asparagine.....	38.7	29	13.4	76	17.6	68
Beef extract.....	39.1	28	19.4	64	17.1	69
Peptone.....	33.5	38	18.7	66	20.3	63
Casein.....	30.5	44	19.1	65	13.8	75

* Declo loam only used.

† Per 100 gm. of soil.

TABLE 5

*Effect of energy source on the production of soil-aggregating substances by a Bacillus subtilis species**

INCUBATION days	STERILE MEDIUM 0		10		20	
	Unaggre- gated silt + clay	Aggre- gation	Unaggre- gated silt + clay	Aggre- gation	Unaggre- gated silt + clay	Aggre- gation
	gm.†	per cent	gm.†	per cent	gm.†	per cent
Check—distilled water.....	40.9	25	40.3	26	40.8	25
Dextrose.....	37.2	31	29.8	45	26.7	51
Maltose.....	26.8	50	20.9	62	23.5	57
Xylose.....	37.6	31	34.1	38	26.6	51
Arabinose.....	39.2	28	31.7	42	31.2	43
Sucrose.....	38.6	29	17.6	68	12.9	76

* Declo loam only used.

† Per 100 gm. of soil.

this, the material from the dextrose was not nearly so effective in aggregating the soils as that from sucrose. This would tend to indicate that the aggregating materials from the two sugars were different in nature or that the residual dextrose interfered with the effectiveness of the active material more than did the residual sucrose.

NATURE OF ACTIVE MATERIAL

In order to ascertain to some extent the nature of the aggregating principle produced by the soil bacillus, 10-day incubated media containing either NaNO_3 or asparagine as the nitrogen source were utilized. The cultures were centrifuged to remove the bacterial cells and dialyzed in running tap water for 48 hours to remove residual sugar and other soluble compounds. The remaining suspensions were analyzed for dry weight, ash, carbon by chromic acid digestion, and nitrogen by the Kjeldahl procedure. Table 6 presents the results. The low nitrogen and the carbon content of the crude preparation suggested that the material was primarily a polysaccharide. Further to substantiate this assumption, the material was tested for its ability to reduce Fehling's solution both before and after hydrolysis with 2 per cent HCl . Before hydrolysis no reduction occurred. After hydrolysis the reaction was positive, indicating that the substance was a polysaccharide synthesized by the soil bacillus.

TABLE 6

*Chemical analyses of a soil-aggregating substance synthesized by a Bacillus subtilis species**

MEDIUM	ASH	CARBON	NITROGEN	REDUCTION OF FEHLING'S SOLUTION	
				Before hydrolysis	After hydrolysis†
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		
NaNO_3 -sucrose	7.1	42.6	0.13	Negative	Positive
Asparagine-sucrose	6.6	41.6	0.40	Negative	Positive

* Analyses made on a crude suspension of the material in tap water.

† Hydrolysis with 2 per cent HCl .

When a solution of the polysaccharide was slowly added to alcohol a gummy, stringy, very sticky precipitate was formed. Some of the material, however, remained in suspension in the form of a milky precipitate. Upon standing, the portion that remained in suspension formed a thin, tough membrane over the entire inner surface of the glass container. The gummy precipitate when washed with absolute alcohol, followed by ether, and dried at 55°C ., was hard and appeared horny but could be broken and ground to a powder with a mortar and pestle. It thus appeared that the substance was a hemicellulose-like polysaccharide.

To ascertain whether sucrose was necessary for the production of a polysaccharide by the bacillus or whether other energy sources could be utilized, the organism was cultured in xylose, arabinose, sucrose, maltose, dextrose, and starch media. After incubation for 15 days all the media were filtered through paper into alcohol. In all instances a precipitate was formed. Inasmuch as starch is itself a polysaccharide and gives a precipitate in alcohol, the precipitate formed from the inoculated starch medium was compared with that from the sterilized medium. The inoculated medium gave a gummy precipitate, whereas the ster-

ile medium produced a white, powdery precipitate. The precipitates were thrown out of suspension by centrifuging, washed with alcohol several times, and redissolved in water. The precipitate from the sucrose medium went into solution slowly in cold water. Boiling hastened the process. The other precipitates were readily soluble in cold water. In each case half the suspension was tested for reduction of Fehling's solution. The remaining portion was hydrolyzed with 2 per cent HCl for 5 hours in flowing steam and then tested for the presence of reducing sugars. All tests before hydrolysis were negative. After hydrolysis all were positive. The greatest amount of precipitate and the strongest tests with Fehling's solution occurred with the sucrose and dextrose media.

These tests indicate that the soil bacillus produces a polysaccharide from all the energy materials tested.

UTILIZATION OF POLYSACCHARIDE BY MICROBES

A medium in which a very small amount of egg albumin was used as the nitrogen source and the polysaccharide produced by the soil bacillus as the source of carbon was prepared in order to determine whether or not various soil microbes could destroy it. A similar medium containing glucose as the energy material was used for comparison. Plate counts in replications of six for bacteria and actinomycetes were made on Palouse silt loam. Several microbes were also streaked on plates of both media. The number of actinomycetes per gram of soil developing on the plates of both media was approximately the same (11,000,000). The dextrose medium, however, supported the growth of 37 million bacteria per gram of soil compared with 24 million for the bacterial polysaccharide. The streaked dextrose plates supported moderate to heavy growth of *Aspergillus niger*, *Penicillium*, *Rhizopus nigricans*, the antibiotic bacillus, the *B. subtilis* sp., and *Actinomyces coelicolor*. On the other hand, the bacterial polysaccharide supported only a trace to slight growth of the three fungi, moderate growth of the two bacilli, and very heavy growth of the actinomycete.

The persistence of the polysaccharide in the soil was studied. A dialyzed suspension of the material was added to the Declo soil in the usual manner. After drying at 55° C. the soil was moistened to 55 per cent of saturation with distilled water and incubated for 20 and 40 days. Before incubation a 67 per cent aggregation of the silt and clay particles compared to 25 per cent for the control was produced. Only 38 per cent aggregation remained after 20 days' incubation, and this was still further reduced to 32 per cent after 40 days.

It is evident that the substance is readily destroyed by certain members of the soil population.

DISCUSSION

A species of the fungus *Cladosporium*, and a soil bacillus apparently belonging to the *Bacillus subtilis-mesentericus* group, when given a suitable energy source and allowed to develop in sterilized soil, brought about a very marked aggregation of the silt and clay particles of Portneuf sandy loam. When the organisms were cultured in liquid media and the microbial cell substance was removed, the

remaining material still produced marked aggregation in the case of the bacillus, but only moderate aggregation in the case of the fungus. Calculated on the basis of the dispersed silt + clay particles aggregated, the fungus when grown in the soil brought about 57 per cent aggregation after 3 weeks' incubation. When cultured in liquid medium for 10 days and the pads removed, the remainder of the culture containing substances produced by the fungus brought about approximately 32 per cent aggregation. This figure was reduced to 16 per cent after 20 days' incubation. From calculations based on these figures one might assume that 28 to 55 per cent of the binding effect produced in the soil culture was brought about by decomposition products or substances synthesized by the fungus and that the remaining portion was due to the mechanical binding of the soil particles by the tough mycelial network formed throughout the soil mass by the fungus. On the other hand, as indicated by the fact that aggregating substances produced by the fungus in the liquid-medium were gradually destroyed, it is possible that some of the same substances produced in the soil may have been rendered resistant to further decomposition by physicochemical union with certain soil constituents. If such were the case, an even greater percentage of the aggregating effect could be ascribed to cementing substances formed during the metabolic activities of the fungus cells.

In the case of the soil bacillus the following calculations can be made: Declo loam contained approximately 40.6 per cent of dispersed silt + clay particles. In other words, every 100 gm. of soil contained 40.6 gm. of silt + clay that was in a dispersed condition, or in aggregates less than $50\ \mu$ in diameter. The combined cells and substances produced by them from 2 gm. of sucrose, when added to 100 gm. of the soil, aggregated 28.7 gm. of the dispersed silt + clay fraction. The cells alone bound 6.4 gm., and the substances produced by the cells, 23.7 gm. The sum of the last two figures is 30.1 gm., which is very close to the total soil aggregated by the combined cells and their products. Other series gave even closer results. It is thus reasonably safe to assume that approximately 20 per cent of the aggregating effect of the bacillus was due to the cells and that 80 per cent was brought about by aggregating materials produced by the cells.

A substance synthesized by the soil bacillus and which was primarily responsible for the binding effect appeared to be a hemicellulose-like polysaccharide. Microbial polysaccharides, commonly referred to as microbial gums or hemicellulose-like substances, are synthesized by a variety of organisms. Many bacteria, fungi, and some yeasts have been reported to produce these substances (4, 5, 6, 13, 17). These gummy products are usually named according to the sugars they yield upon hydrolysis with dilute acids. For example, those yielding dextrose are called "dextrans"; those yielding galactose, "galactans," etc. Some are more or less complex substances yielding two or more sugars, and often uronic acids. Those yielding primarily uronic acids are referred to as polyuronides.

Several investigators have studied the production of gummy products by organisms belonging to the *Subtilis-mesentericus* group. In all instances a polysaccharide was synthesized from sucrose and raffinose only, and the organisms had to be supplied with organic nitrogen (4, 5, 6, 13). The organism used in

the studies reported in this paper differs from those reported in the literature in that a hemicellulose-like substance is produced from common sugars other than sucrose, and inorganic as well as organic nitrogen is utilized as a nitrogen source. Whether or not the organism synthesized the same gummy product from the various sugars tested, or whether different polysaccharides are formed is not known at this time. Studies designed to determine more specifically the nature of the polysaccharides produced are under way and will be reported in another paper.

The polysaccharide synthesized from sucrose by the *B. subtilis* sp. was a very effective soil-aggregating agent. Only 0.3 gm. (0.3 per cent) of the material when incorporated into 100 gm. of soil brought about from 68 to 81 per cent aggregation of the silt and clay particles. Inasmuch as this fraction of the soil in the controls was already 25 per cent aggregated, this would represent 57 to 75 per cent aggregation of the dispersed silt + clay. The Declo soil contained 54.4 per cent total silt + clay and approximately 41 per cent dispersed silt + clay. A 75 per cent aggregation of the dispersed silt and clay would mean that approximately 31 gm. of the 41 were bound into water-stable aggregates larger than 50 μ in diameter. When it is considered that many of the well-aggregated soils in the nonlateritic sections of the country contain 3 to 6 per cent organic matter, the effectiveness of this material is apparent.

The aggregating material produced by the soil bacillus does not persist in the moist soil. Fungi attack it only to a very slight degree, but it is readily destroyed by many bacteria and actinomycetes. Consequently it belongs to the group of aggregating substances which are formed during the more or less rapid decomposition of organic materials and only temporarily contributes to increased soil aggregation. Indirectly it could contribute to improved soil structure by acting as an energy source for various microbes which, in turn, could synthesize soil-aggregating substances of a different nature.

Although the hemicellulose-like, soil-aggregating complex under consideration is readily destroyed in the soil, it is very probable that other substances of a similar nature are synthesized by various microbes and that some of these materials are resistant to microbial attack or undergo certain physicochemical combinations with other soil fractions and are thus rendered resistant. Under such conditions microbial hemicellulose-like "slimes and gums" could play a major role in soil granulation. Most plant hemicelluloses are readily decomposed by microorganisms. When plant residues are incorporated into the soil the hemicellulose fraction is immediately attacked and begins to disappear more rapidly than the more resistant cellulose. As decomposition continues, however, the concentration of hemicelluloses reaches a certain level at which it no longer rapidly disappears. The celluloses, on the other hand, almost entirely disappear (16, 17). This has been explained by the fact that certain plant hemicelluloses are resistant to decomposition and that considerable quantities of hemicelluloses in the form of bacterial and fungal "slimes and gums" are synthesized by the microorganisms concerned in the decomposition process. Some of the so-called microbial gums are believed to be resistant to decomposition (17). Many of

these synthetic products are polyuronides. Norman and Bartholomew (14) suggest that uronic residues in soil may be stabilized by the association or combination with some other organic or inorganic material. On the basis of total reducing sugars present after hydrolysis with 2 per cent HCl, it was found that the organic matter of soils contained as much as 11 per cent hemicelluloses (17). Norman and Bartholomew (14) determined the uronide groupings in the organic matter of a large number of soils by measuring the production of CO₂ upon hydrolysis with 12 per cent HCl. From 10 to 15 per cent of the total organic carbon of surface soils was found to be present in the uronide form. In the subsoils the proportion of uronide carbon was much greater. It is, therefore, very probable that a considerable proportion of the organic matter of most soils is present in the form of hemicelluloses or hemicellulose-like polysaccharides. This being the case, it is very probable that these compounds contribute substantially toward the state of aggregation of the soil.

SUMMARY

Two soil microbes, a fungus belonging to the *Cladosporium* group, and an aerobic bacillus, apparently belonging to the *Bacillus subtilis-mesentericus* group, were found to bring about marked aggregation of the silt and clay particles of the soil. Up to 50 per cent of the aggregating effect of the fungus was brought about by substances produced by the cell material, and the remainder was due to the binding influence of the fungus mycelium. The soil bacillus cells, on the other hand, produced 20 per cent of the aggregating effect, and substances produced by the cells accounted for 80 per cent.

A hemicellulose-like polysaccharide synthesized by the soil bacillus was found to be primarily responsible for the marked aggregating effect. The organism synthesized a polysaccharide and brought about marked soil aggregation when supplied with either organic or inorganic nitrogen and when dextrose, maltose, xylose, arabinose, or sucrose was utilized as energy material. The greatest aggregation and greatest production of polysaccharide occurred with sucrose.

The active aggregating material was attacked to a limited extent by fungi, but was readily destroyed by certain bacteria and actinomycetes. It therefore belongs to the class of microbial aggregating agents which only temporarily contribute to increased soil aggregation.

REFERENCES

- (1) ALDERFER, R. B., AND MERKLE, F. G. 1941 The measurement of structural stability and permeability and the influence of treatments upon these properties. *Soil Sci.* 51: 201-212.
- (2) BROWNING, G. M. 1938 Changes in erodibility of soils brought by application of organic matter. *Soil Sci. Soc. Amer. Proc.* 2: 85-96.
- (3) BROWNING, G. M., AND MILAM, F. M. 1944 The effect of different types of organic materials and lime on soil aggregation. *Soil Sci.* 57: 91-106.
- (4) COOPER, E. A., AND PRESTON, J. F. 1935 Enzyme formation and polysaccharide synthesis by bacteria. *Biochem. Jour.* 29: 2267-2277.
- (5) HARRISON, F. C., TARR, H. L. A., AND HIBBERT, H. 1930 Studies on reactions relating to carbohydrates: XXXIII. The synthesis of polysaccharides by bacteria and enzymes. *Canad. Jour. Res.* 3: 449-463.

- (6) HIBBERT, H., TIPSON, R. S., AND BRAUNS, F. 1931 Studies on reactions relating to carbohydrates and polysaccharides: XXXIV. The constitution of levan in its relation to inulin. *Canad. Jour. Res.* 4: 221-239.
- (7) MCCALLA, T. M. 1942 Influence of biological products on soil structure and infiltration. *Soil Sci. Soc. Amer. Proc.* 7: 209-214.
- (8) McHENRY, J. R., AND RUSSELL, M. B. 1944 Microbial activity and aggregation of mixture of bentonite and sand. *Soil Sci.* 57: 351-357.
- (9) MARTIN, J. P., AND WAKSMAN, S. A. 1941 Influence of microorganisms on soil aggregation and erosion: II. *Soil Sci.* 52: 381-394.
- (10) MARTIN, J. P. 1942 The effect of composts and compost materials upon the aggregation of the silt and clay particles of Collington sandy loam. *Soil Sci. Soc. Amer. Proc.* 7: 218-222.
- (11) MARTIN, T. L., AND ANDERSON, D. A. 1942 Organic matter decomposition, mold flora, and soil aggregation relationships. *Soil Sci. Soc. Amer. Proc.* 7: 215-217.
- (12) MEYERS, H. F., AND MCCALLA, T. M. 1941 Changes in soil aggregation in relation of bacterial numbers, hydrogen-ion concentration, and length of time soil was kept moist. *Soil Sci.* 51: 189-200.
- (13) NORMAN, A. G. 1937 *The Biochemistry of Cellulose, the Polyuronides, and Lignin.* Oxford University Press, London.
- (14) NORMAN, A. G., AND BARTHOLOMEW, W. V. 1943 The chemistry of soil organic matter: I. Distribution of uronic carbon in some soil profiles. *Soil Sci.* 56: 143-150.
- (15) PEELE, T. C. 1940 Microbial activity in relation to soil aggregation. *Jour. Amer. Soc. Agron.* 32: 204-212.
- (16) TENNEY, F. G., AND WAKSMAN, S. A. 1929 Composition of natural organic materials and their decomposition in the soil: IV. The nature and rapidity of decomposition of the various organic complexes in different plant materials, under aerobic conditions. *Soil Sci.* 28: 55-83.
- (17) WAKSMAN, S. A. 1938 *Humus.* The Williams & Wilkins Company, Baltimore.
- (18) WAKSMAN, S. A., AND MARTIN, J. P. 1939 The role of microorganisms in the conservation of the soil. *Science* (n.s.) 90: 304-305.
- (19) WOODRUFF, C. M. 1940 Variations in the state and stability of aggregation as a result of different methods of cropping. *Soil Sci. Soc. Amer. Proc.* 4: 13-18.

RETENTION OF PHOSPHATES BY SOILS: II. EFFECT OF DRYING AND OF CERTAIN CATIONS AND ANIONS ON THE CATION-EXCHANGE CAPACITY OF SOILS¹

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In a recent paper (7) it was shown that additions of ferric and aluminum chloride to virgin Hammond very fine sandy loam affected the retention by the soil of subsequently added phosphates; and that the relation of the amounts of phosphorus soluble in water, CO₂-aspirated water, and 0.002 *N* H₂SO₄ at pH 3.1 to the reaction of the treated soils indicated the chemical nature of the phosphatic compounds formed. It was further found (7, 8) that the critical points in the pH-solubility curves for the phosphates agreed with the solubilities of comparable mixtures in aqueous solutions as worked out by Gaarder (11) but that the magnitude of the solubilities indicates that the effect of the iron and aluminum upon phosphate retention by the soil functions through the soil colloidal fraction. Data which indicated that most of the added iron and aluminum entered the base-exchange complex of the soil were also obtained.

Since Pierre and Scarseth (29) had found low base-exchange capacities of extracted soil colloids to be associated with low silica-sesquioxide ratios of the colloids, and Mattson (23) had shown that the exchange capacity of artificially precipitated and natural soil colloids, at pH 7.0, increases with the proportion of acidoid (SiO₂, P₂O₅, humus) to ampholytoid (sesquioxides), the question arose as to whether or not the iron and aluminum that had entered the exchange complex of the soil was replaceable. The experimental work reported herein was undertaken with the specific objective of answering this question and to obtain further information regarding the chemical nature of phosphate fixation by soils.

REVIEW OF LITERATURE

Since the original work by Way (39, 40), who has been credited (19, 22) with being the first to demonstrate the capacity of soils to exchange bases, many contributions have been made concerning the nature of the exchange complex and the principles involved in accurately measuring the exchange capacity of soils.

Hendricks and Fry (13) showed that the finely divided materials of soils contained crystalline substances and from comparison of powder diffraction photographs decided that the common mineral constituents of soil colloids were montmorillonite-beidellite, ordovician bentonite (or a mixture of montmorillonite and quartz), and halloysite. Kelly *et al.* (20, 21) also concluded that the base-exchange material of clay minerals is crystalline and showed that these minerals retained replaceable bases both on their interior and exterior surfaces. Jackson and Truog (14) found by grinding soil colloids 2 to 14 days that the colloidal particles were reduced to nearly molecular size and that as a result of this

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size of particle, silica and alumina became relatively soluble in dilute acids, dilute Na_2CO_3 solution, and neutral salt solutions. They also obtained a high but very unstable base-exchange capacity and observed, "The base exchange capacity of soil has its origin in the exchange bonds of particles of colloidal size which are relatively stable towards chemical action."

Numerous investigators have published data on the chemical and physical factors affecting the fixation or release of potassium by soils. Peech and Bradfield (28) reviewed the literature and defined the chemical principles by which most of the seemingly conflicting data on the influence of lime and magnesia on soil potassium and on the absorption of potassium by plants can be explained.

Several observers (3, 15, 33, 38, 41, 42) have noted that drying or alternate wetting and drying increased or accelerated the absorption of potassium in a nonreplaceable form by soils. Others (1, 10, 35, 42) have obtained an increase of exchangeable potassium in soils as the result of moistening, freezing, and thawing, or of the decomposition of plant material such as may occur under field conditions. The possible relationships between such changes in replaceable and nonreplaceable cations and changes in the total exchange capacity of the soil were not completely worked out.

Joffe and Kolodny (16) noted that "Kolodny³ reported that the phenomenon of potassium fixation in bentonite is accompanied by a decrease in exchange capacity which is equivalent to the potassium fixed." In later work with soils, Joffe and Levine (17) found that potassium fixation was usually accompanied by a decrease in exchange capacity, but the relationship was random and not equivalent. They also found that fixation in nonreplaceable form, as measured by leaching with ammonium acetate, was peculiar to potassium and that the cations Na, Ca, Mg, Ba, and Sr did not appear to be nonreplaceably fixed. DeTurk and others (9, 41) obtained data which support the belief that the reactions "I Primary mineral K \rightarrow II Fixed potassium (Acid-insoluble K \rightleftharpoons Acid-soluble K) \rightleftharpoons III Replaceable K \rightleftharpoons IV Water-soluble potassium" maintain a slowly shifting equilibrium.

Equivalent replacement of the exchangeable basic cations of soils is known to be relatively rapid. Because of the difficulty in replacing hydrogen with neutral salts, its determination is less accurate. Parker (27) showed that similar results for exchangeable hydrogen could be obtained by different methods if sufficient time was allowed for equilibrium to be established and the end-point reaction resulting from the treatments, i.e., leaching or titration, was comparable. Several methods for determining the cation-exchange properties of soils with salt solutions adjusted to near the neutral point, pH 7.0, have been developed. Since an appreciable amount of hydrogen is present in soils at pH 7.0 and a soil reaction of about pH 8.3 is characteristic of soils saturated with calcium and of naturally calcareous soils (5), there has been a trend to adopt the latter reaction in solutions for measuring the cation-exchange properties of soils. It would seem that if a larger amount of exchangeable hydrogen is obtained by one method than by another, a correspondingly larger cation-exchange capacity would also be obtained.

There are a limited number of references to the possible effect of anions upon the cation-exchange capacity of soils. In 1935 Mattson and Hester (24) wrote: "When the soil complex reacts with the common, easily displaced ions, the process is reversible and the complex is left intact, retaining its identity, its isoelectric point, and its exchange capacity. When other ions which form very slightly dissociated combinations react with the soil complex, the latter changes its character and behavior. Such strongly associated ions become a part of the colloidal ion complex and modify its properties by changing the strength and magnitude of the acidic and basic residues." Toth (36) in 1937 observed that silicate- and phosphate-treated colloids exhibited a marked increase in exchange capacity and a reduction in ultimate pH. In later work (37) with colloids from the Colts Neck and Sassafras series, he obtained data on the absorption of phosphates from mixtures

³ Kolodny, L. The mechanism of potassium fixation in soils and the availability of fixed potassium to plants. 1938. [Unpublished doctoral thesis. Copy on file, Rutgers University Library, New Brunswick, N. J.]

of H_2PO_4 and NH_4OH which indicated that "completely deferrated" colloids may adsorb phosphates without altering the cation-exchange capacity. Ravikovitch (30) in studying the effect of exchangeable cations on the availability of phosphates in soils noted that the availability of the PO_4 adsorbed by the II-complex is low, and its liberation, by leaching with 0.05 N HCl , is associated with the partial destruction of the complex.

EXPERIMENTAL PROCEDURE

The 50-gm. samples of Hammond very fine sandy loam that had been previously treated (7, p. 460) were used for most of these experiments. They had been stored in a thoroughly air-dried condition in open beakers in a covered cardboard box for a period lasting from 12 to 14 months after the original equilibration treatment. Ten-gram portions of these air-dried soils were weighed into 250-ml. Erlenmeyer flasks. To each was added 125 ml. of 0.1 N barium acetate having a reaction of pH 8.3, and the contents were shaken intermittently by hand for 30 minutes. They were filtered with a moderate suction on prepared asbestos mats in Gooch crucibles. An additional 125 ml. of the 0.1 N BaAc_2 was used for washing all the soil particles from the original Erlenmeyer to the Gooch crucible and for additional leaching of the soil sample. Suction was continued until the excess BaAc_2 solution was removed but was stopped promptly to avoid drawing air through the still wet sample.

The exchangeable hydrogen was determined by titrating the leachates back to the original pH of 8.3 using cresol red as the indicator and a 250-ml. portion of the original 0.1 N BaAc_2 solution as a standard of comparison for obtaining the end point.

While still wet, the leached samples were washed with six 15-ml. portions of 80 per cent ethyl alcohol. Suction was continued until the soil was almost dry. The samples were transferred to 500-ml. Erlenmeyer flasks and shaken for 30 minutes with 250 ml. of 0.05 N HCl . After filtration, the barium content of duplicate aliquots and the dilute HCl extract was determined by precipitating with saturated K_2SO_4 solution, filtering, and igniting the BaSO_4 to constant weight. The cation-exchange capacity was calculated from the amount of BaSO_4 obtained.

The reactions of these soil samples were also determined at the time the foregoing determinations were made. The pH was measured with a Beckmann electrometer on samples that had been allowed to stand overnight in 1:5 suspensions with distilled water.

EXPERIMENTAL RESULTS

The experimental data on the reaction, the cation-exchange capacity, and the exchangeable hydrogen of the previously treated samples of virgin Hammond very fine sandy loam are given in table 1. The relation of the base exchange capacity of these samples to soil reaction is shown in figure 1. The pH is plotted to show the direct relationship between increase in cation-exchange capacity and hydroxyl-ion concentration.

As shown by the data in table 1, the cation-exchange capacity is not a constant regardless of treatment. It was markedly increased in all series by the additions of $\text{Ca}(\text{OH})_2$, regardless of whether or not $\text{Ca}(\text{OH})_2$ was added in

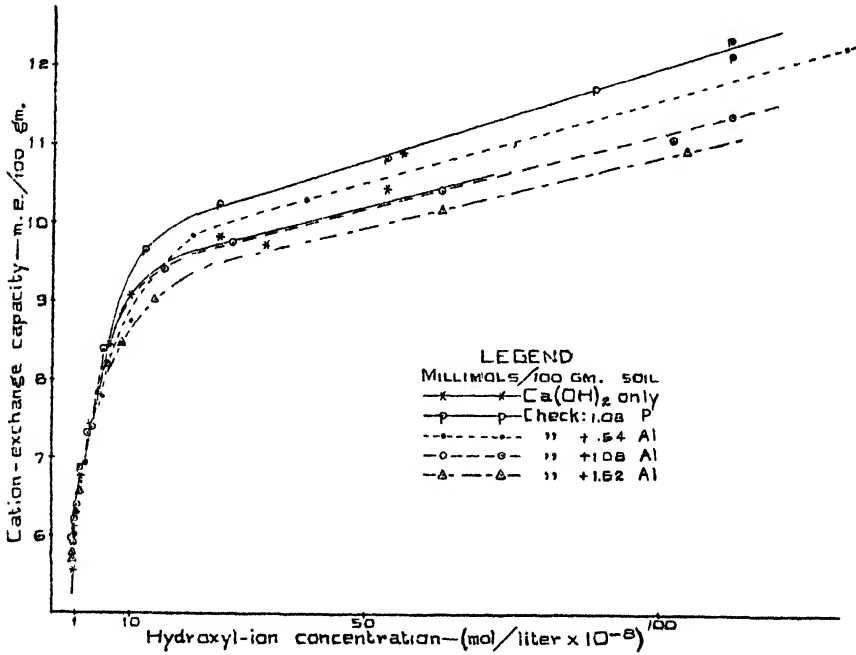
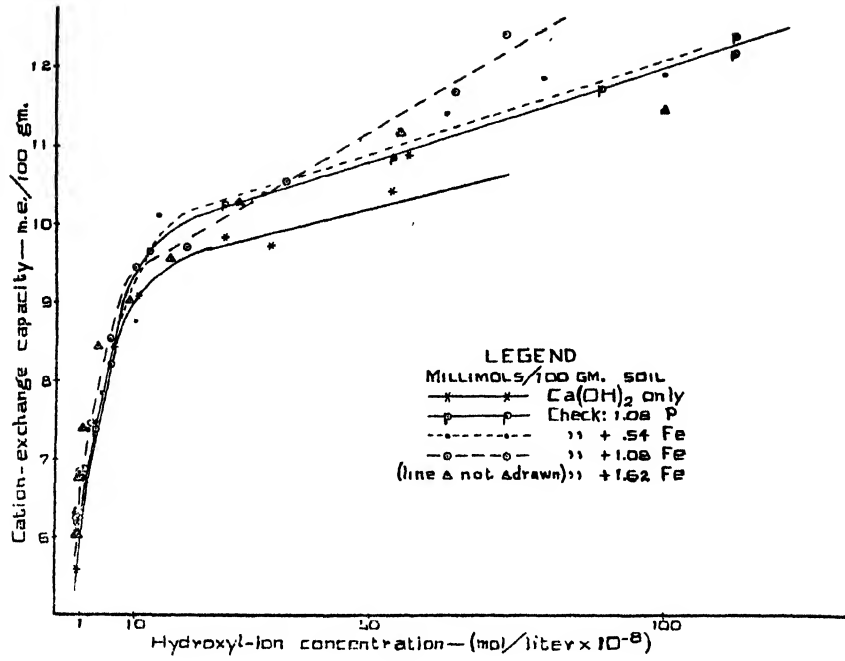


FIG. 1. RELATION OF CATION-EXCHANGE CAPACITY TO OH-ION CONCENTRATION OF SOIL

quantities sufficient to form free carbonates upon being brought into equilibrium with the air. The curves in figure 1 indicate that the increase in cation-exchange capacity produced by liming has a direct linear relationship to the hydroxyl-ion

TABLE 1

Reaction, cation-exchange capacity, and exchangeable hydrogen of treated samples of virgin Hammond very fine sandy loam*

Ca (OH) ₂ added . Sample number.	m.e.	0	2.16	4.32	6.48	8.64	10.80	12.96	15.12	17.28	19.44
		1	2	3	4	5	6	7	8	9	10
<i>Reaction—pH determined December 8, 1943</i>											
No treatment besides Ca(OH) ₂	..	5.30	5.75	6.22	6.5	6.8	7.02	7.52	7.4	7.73	7.75
0.54† mmol Ca(H ₂ PO ₄) ₂ ·H ₂ O- check		5.85	6.18	6.53	6.78	7.1	7.40	7.73	7.95	8.05	8.05
Check + 0.54 mmol FeCl ₃ ·6H ₂ O		5.4	5.95	6.32	6.65	7.0	7.18	7.5	7.8	7.9	8.0
Check + 1.08 mmols FeCl ₃ ·6H ₂ O		4.9	5.4	5.95	6.4	6.74	7.0	7.28	7.55	7.81	7.9
Check + 1.62 mmols FeCl ₃ ·6H ₂ O		4.65	5.0	5.66	6.02	6.55	6.95	7.2	7.44	7.74	8.0
Check + 0.54 mmol AlCl ₃ ·6H ₂ O		5.42	5.93	6.4	6.73	7.0	7.31	7.6	7.78	8.12	8.14
Check + 1.08 mmols AlCl ₃ ·6H ₂ O		5.0	5.6	6.06	6.46	6.75	7.2	7.44	7.8	8.01	8.05
Check + 1.62 mmols AlCl ₃ ·6H ₂ O		4.55	5.02	5.65	6.25	6.67	6.96	7.15	7.8	8.02
<i>Cation-exchange capacity—m.e./100 gm. soil</i>											
No treatment besides Ca(OH) ₂		5.57	6.13	6.77	7.43	8.44	9.08	9.72	9.83	10.41	10.9
0.54† mmol Ca(H ₂ PO ₄) ₂ ·H ₂ O- check		6.21	6.88	7.37	8.2	9.64	10.22	10.82	11.7	12.34	12.12
Check + 0.54 mmol FeCl ₃ ·6H ₂ O		6.06	6.83	7.37	7.84	8.74	10.11	10.39	11.4	11.85	11.89
Check + 1.08 mmols FeCl ₃ ·6H ₂ O		6.17	6.25	6.83	7.45	8.53	9.45	9.7	10.58	11.67	12.42
Check + 1.62 mmols FeCl ₃ ·6H ₂ O		6.28	6.08	6.77	7.39	8.46	9.02	9.57	10.28	11.16	11.42
Check + 0.54 mmol AlCl ₃ ·6H ₂ O		6.0	6.3	6.92	7.78	8.74	9.83	10.32	11.4	11.74	12.38
Check + 1.08 mmols AlCl ₃ ·6H ₂ O		5.95	5.93	6.4	7.3	8.38	9.42	9.75	10.41	11.07	11.37
Check + 1.62 mmols AlCl ₃ ·6H ₂ O		5.8	5.7	6.0	6.58	7.84	8.46	9.02	.	10.17	10.95
<i>Exchangeable hydrogen—m.e./100 gm. soil</i>											
No treatment besides Ca(OH) ₂	..	3.94	2.95	2.26	1.87	1.33	0.94	0.59	0.39	0.20	0.10
0.51† mmol Ca(H ₂ PO ₄) ₂ ·H ₂ O- check		3.43	2.58	1.99	1.49	1.14	0.69	0.35	0.20	0.10	0.10
Check + 0.54 mmol FeCl ₃ ·6H ₂ O		4.02	3.18	2.58	1.89	1.34	0.99	0.50	0.40	0.15	0.15
Check + 1.08 mmols FeCl ₃ ·6H ₂ O		1.67	3.67	3.08	2.38	1.69	1.34	0.84	0.55	0.25	0.15
Check + 1.62 mmols FeCl ₃ ·6H ₂ O		5.06	4.17	3.77	3.08	2.13	1.54	0.99	0.64	0.35	0.20
Check + 0.54 mmol AlCl ₃ ·6H ₂ O		3.92	2.98	2.38	1.79	1.24	0.89	0.50	0.3	0.10	0.10
Check + 1.08 mmols AlCl ₃ ·6H ₂ O		4.72	3.67	2.98	2.18	1.64	1.09	0.74	0.35	0.15	0.20
Check + 1.62 mmols AlCl ₃ ·6H ₂ O		4.92	4.27	3.57	2.68	2.03	1.49	0.89	0.30	0.20

* All treatments given are for 100 gm. soil.

† 0.54 mmol Ca(H₂PO₄)₂·H₂O supplies 1.08 mmols PO₄.

concentration. A significant break in the relationship occurs in all series at a reaction of pH 7.0-7.3.

Effect of drying

With the object of determining whether the observed variations in cation-exchange capacity were due to the specific effect of drying the filtered soils from the H₂O-Ca(OH)₂-soil-CO₂-air samples, some additional series were run. The soil was the same as that previously used but was collected from the same

location in the field at a later date. The procedure was varied in the different series. In one series the cation-exchange properties were determined immediately after filtering and without allowing the soils to become dry. In another, CO_2 was bubbled through the suspensions for 30 minutes immediately after the soil was added. In still another series the cation-exchange capacity of duplicate samples was determined by both the barium acetate and ammonium acetate (6) methods. The data are given in table 2.

As shown by the data in table 2, differences were obtained in the cation-exchange capacity in all series. The addition of lime produced large increases in the cation-exchange capacity regardless of whether the samples were air-dried or not. The data indicate that air-drying may reduce the cation-exchange capacity of moderately acid soils having a low degree of base saturation by as much as 10 to 12 per cent of the value obtained by this method.

TABLE 2

Cation-exchange properties per 100 gm. soil as affected by different procedures and methods

SAMPLE NO.	Ca(OH) ₂ USED PER 100 GM. SOIL	DEGREE OF CALCIUM ABSORPTION CAPACITY	SAMPLES NOT ALLOWED TO AIR-DRY AFTER EQUILIBRATION				SAMPLES FILTERED AND AIR-DRIED FOR 14 DAYS AFTER EQUILIBRATION			
			Soil in contact with Ca(OH) ₂ overnight		Carbonated upon addition of soil		Determinations by barium acetate method		Determinations by ammonium acetate method	
			Cation-exchange capacity	Exchangeable hydrogen	Cation-exchange capacity	Exchangeable hydrogen	Cation-exchange capacity	Exchangeable hydrogen	Cation-exchange capacity	Increase over Ba(Ac) ₂ method
	m.e.	per cent	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
1	0	0	7.48	2.95	7.67	3.84	7.22	4.68	6.57	0.65
2	2.16	20	8.12	2.95	7.84	3.05	7.52	3.22	6.69	0.83
3	4.32	40	8.31	2.07	8.42	2.36
4	6.48	60	8.87	1.23	8.93	1.48	8.65	1.46	7.34	1.31
5	8.64	80	9.77	0.74	9.77	0.79
6	10.80	100	10.86	0.39	10.80	0.39	10.41	0.49	7.85	2.56
7	12.96	120	11.50	0.20	11.48	0.30
8	15.12	140	12.62	0.10	12.00	0.20	11.67	0.10	8.18	3.49
9	17.28	160	13.63	0.0	12.00	0.15
10	19.44	180	12.70	0.15

The variations in the values obtained for the cation-exchange capacity of comparable samples shown in table 1 and in columns 4, 6, and 8 of table 2 suggest that complete cation replacement was not obtained. Consequently the cation-exchange properties of a uniformly mixed soil sample were determined with different volumes and concentrations of barium acetate solution. The values obtained are given in table 3.

The data in table 3 show that 125 ml. of 0.1 N barium acetate solution shaken with 10 gm. soil, plus 125 ml. leachate, fails to replace all the cations or to saturate the exchange complex with barium. They further indicate that complete cation replacement was not obtained even with 750 ml. of 0.1 N or 250 ml. of N solution. Although complete replacement is not obtained by the method, the magnitude of the differences for the duplicate samples indicates that reasonably accurate, but not exact, duplicate values are obtained.

Effect of calcium

The data in table 2 show that, even when the samples were not air-dried, large differences in cation-exchange capacity occurred as the result of liming.

The amounts of $\text{Ca}(\text{OH})_2$ added to the successive samples of each series in tables 1 and 2 were based upon the capacity of the soil to absorb calcium (7). The point of saturation of the soil with calcium was determined by the equilibration method described by Bradfield and Allison (5). The free carbonates were measured with the apparatus and procedure described by Schollenberger (32). Thus in tables 1 and 2 the sample designated as No. 6 in all series had just sufficient $\text{Ca}(\text{OH})_2$ added to saturate the soil with calcium. Samples 7 to 10, inclusive, had an excess of $\text{Ca}(\text{OH})_2$ added, which theoretically was converted to free carbonates when the H_2O - $\text{Ca}(\text{OH})_2$ -soil systems were brought to equilibrium with the air.

TABLE 3

Effect of the volume and concentration of barium acetate solution upon the values obtained for cation-exchange capacity and exchangeable hydrogen

SAMPLE NO.*	Ba(C ₂ H ₃ O ₂) ₂ · H ₂ O SOLUTION USED			CATION-EXCHANGE CAPACITY <i>m.e./100 gm.</i>	EXCHANGE-ABLE HYDROGEN <i>m.e./100 gm.</i>	DEGREE BASE SATURATION <i>per cent</i>	AV. INCREASE IN EXCHANGE CAPACITY	
	Conc.	Volume	Reaction					
	<i>N</i>	<i>ml</i>	<i>pH</i>				<i>m.e./100 gm</i>	<i>per cent</i>
1	0.1	750	8.35	8.38	5.08	39.4	1.56	23
2	0.1	750	8.35	8.40	5.08	39.5		
3	0.1	500	8.35	7.52	4.68	37.8		
4	0.1	500	8.35	7.75	4.87	37.2	0.80	12
5	0.1	250	8.35	6.94	4.26	38.6		
6	0.1	250	8.35	6.73	4.06	39.6	check	100
7	0.5	250	8.25	9.06	5.68	37.3		
8	0.5	250	8.25	9.00	5.48	39.1		
9	1.0	250	8.30	10.24	6.70	34.6	3.37	49
10	1.0	250	8.30	10.17	6.29	38.2		

* Weight of each soil sample, 10 gm.

The data given in table 1 show that the pH value of sample 6 in no series exceeded 7.40. The break in the curves in figure 1 occurs for all series at a reaction between pH 7.0 and 7.3 or just above the experimental value obtained for sample 6 in all series but the monocalcium phosphate check. This pH value for the reaction at which soils become saturated with calcium and above which free CaCO_3 may occur is lower than the value of pH 8.0–8.4 which is often thought of as the equilibrium point.

The curves in figure 1 indicate that the increase in cation-exchange capacity resulting from liming is directly and lineally related to the hydroxy-ion concentration of the systems. This relationship may be due to the reaction of $\text{Ca}(\text{HCO}_3)_2$ with the anion absorbing complex of the soil. One stoichiometric relationship is suggested in the discussion.

The values for cation-exchange capacity as determined with barium acetate were larger than those obtained by leaching with neutral, normal ammonium

acetate. This was expected since both Bower and Truog (4) and Golden, Gammon, and Thomas (12) have shown that the results for exchange capacity when determined with polyvalent cations (Ba^{++}) are significantly higher than when determined by means of monovalent ions (NH_4^+). This effect was ascribed (4) to the formation of basic salts with the relatively weak soil acid. Since, for each increment of lime, barium acetate gave larger values, both real and relative, for the cation-exchange capacity than did ammonium acetate, it would seem that the formation of basic salts by barium increases as the acidity of the soil decreases.

The increase in the value for cation-exchange capacity of the soil samples that were limed beyond their saturation capacity for calcium, as shown by figure 1, is due to the presence of free CaCO_3 . This is substantiated by the data in table 4. Partial double decomposition of the barium acetate and CaCO_3 forms some BaCO_3 , which remains in the soil and produces high values for cation-exchange capacity.

TABLE 4

Effect of free CaCO_3 on the results of cation-exchange capacity determinations made with barium acetate

NO.*	CaCO_3 ADDED	EXCHANGEABLE HYDROGEN	BARIUM SULFATE OBTAINED	CALCULATED CATION- EXCHANGE CAPACITY	AMOUNT BaCO_3 FORMED	FRACTION OF CaCO_3 DECOMPOSED
	mgm.	m.e./100 gm.	mgm.	m e /100 gm.	m e./100 gm.	per cent
1	none	5.46	35.3	7.56	check	check
2	1.0	5.26	35.5	7.60	0.04	20.0
3	43.2	1.29	42.2	9.04	1.48	17.1
4	100.0	0.67	46.7	10.00	2.44	12.2

* Weight of each soil sample, 10 gm. on an over-dry basis.

Effect of iron and aluminum

As shown by the data in table 1 the addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ to the H_2O - $\text{Ca}(\text{OH})_2$ -soil systems resulted, in general, in an increase in the acidity and a decrease in the cation-exchange capacity of the samples. The same was true for the ferric chloride series, with the exception that the samples in each series to which no $\text{Ca}(\text{OH})_2$ was added showed an increase in cation-exchange capacity for the larger quantities of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. These concurrent changes in reaction and exchange capacity of the soil produced by the addition of monocalcium phosphate and ferric or aluminum chloride resulted in only minor differences in the relation of cation-exchange capacity to pH as shown by the curves for the several series in figure 1. At and above the point of saturation with calcium the curves diverge. It should be noted that the differences in the values for the cation-exchange capacity at this point are related to the amounts of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ added and that they all occur at or near the same pH. The data for cation-exchange capacity and pH of the samples to which 1.08 and 1.62 mmols of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were added do not show so clear a relationship as do those from the aluminum series.

The effect of these salts on the cation-exchange capacity only is more clearly shown by the curves in figure 2. These curves show that the addition of mono-calcium phosphate increased cation-exchange capacity in the different series

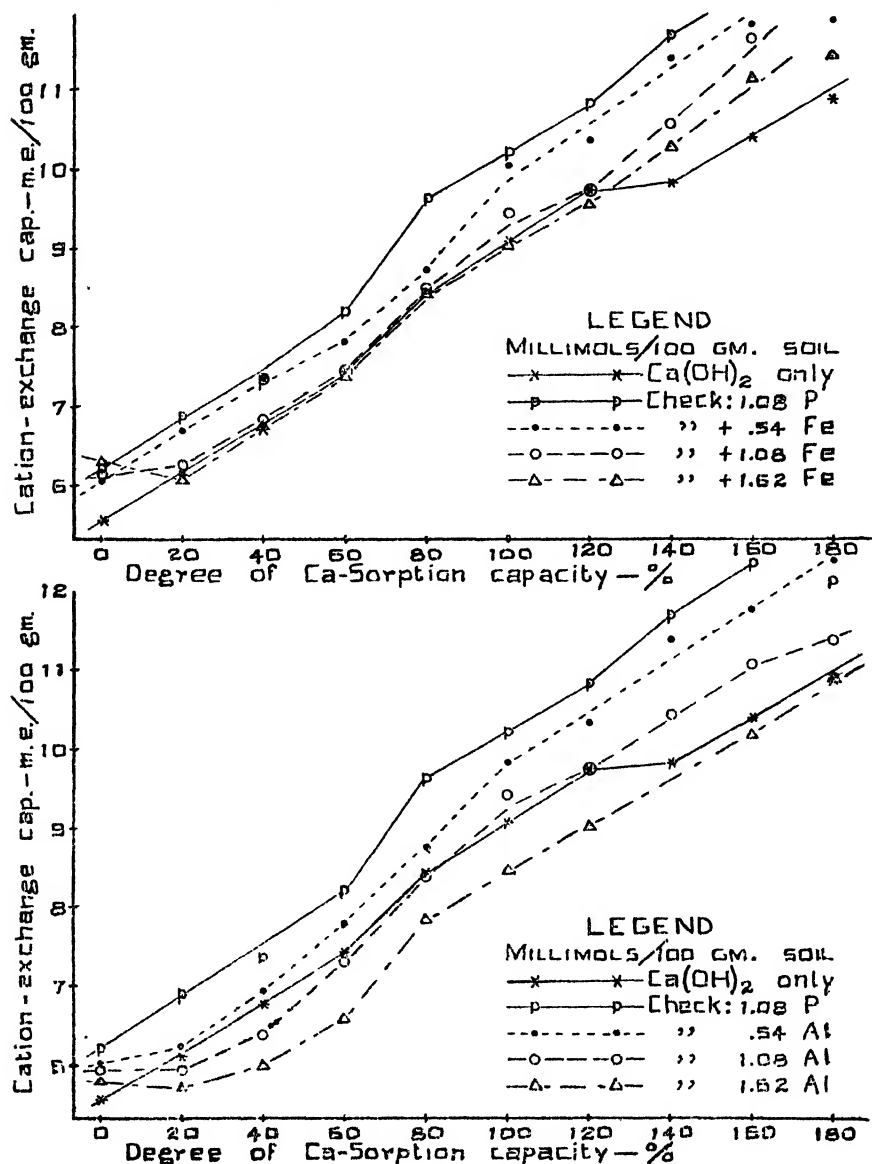


FIG. 2. RELATION OF CATION-EXCHANGE CAPACITY TO AMOUNT OF $\text{Ca}(\text{OH})_2$ ADDED

at the same increments of $\text{Ca}(\text{OH})_2$. The further addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ decreased it. The addition of 1.08 mmols of either ferric or aluminum chloride, which was considered to be equivalent to the phosphate in 0.54

mmols $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, decreased the cation-exchange capacity at reactions below pH 7.5 about as much as the monocalcium phosphate had increased it. In other words, the Fe and Al offset the effect of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ when added in equivalent amounts. The addition of only half as much $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, or 0.54 mmols, tended to reduce the exchange capacity only half as much. The values obtained from the aluminum series approached a chemically equivalent relationship more closely than did those from the iron series. This was also true for the series to which Fe and Al were added in excess, i.e., 1.62 mmols. At this level of added $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ the cation-exchange capacity was reduced to less than those of the original $\text{Ca}(\text{OH})_2$ series in all but the most

TABLE 5

Increases in cation-exchange capacity produced by monocalcium phosphate in relation to the pH of the samples and the probable form of phosphate

SAMPLE NO.	Ca(OH) ₂ ADDED PER 100 GM. SOIL	DEGREE OF CALCIUM ABSORPTION CAPACITY	CATION-EXCHANGE CAPACITY				Ca HELD BY CALCIUM PHOSPHATE	FORM OF CALCIUM PHOSPHATE	SOIL REACTION Soil:H ₂ O = 1:5	
			Ca(OH) ₂ only added	Ca(OH) ₂ + 0.54 mmol Ca (H ₂ PO ₄) ₂ ·H ₂ O added	Increase from phos- phate	Ca(OH) ₂ series			Ca(OH) ₂ + Ca (H ₂ PO ₄) ₂ ·H ₂ O	
	m.e.	per cent	m.e./100 gm.	m.e./100 gm.	m.e./100 gm.	m.e./100 gm.		pH	pH	
1	0	0	5.57	6.21	0.64	0.54	Ca(H ₂ PO ₄) ₂ ·H ₂ O	5.3	5.85	
2	2.16	20	6.13	6.88	0.75	0.54		5.75	6.18	
3	4.32	40	6.77	7.37	0.60	0.54		6.22	6.53	
4	6.48	60	7.43	8.20	0.77	0.54		6.5	6.78	
5	8.64	80	8.44	9.64	1.20	1.08		6.8	7.1	
6	10.80	100	9.08	10.22	1.14	1.08	CaHPO ₄ ·2H ₂ O	7.02	7.4	
7	12.96	120	9.72	10.82	1.10	1.08		7.52	7.73	
8	15.12	140	9.83	11.70	1.87	1.62	Ca ₃ (PO ₄) ₂	7.4	7.95	
9	17.28	160	10.41	12.34	1.93	1.62		7.73	8.05	
0	19.44	180	10.90	12.12	1.22	1.62		7.75	8.05	

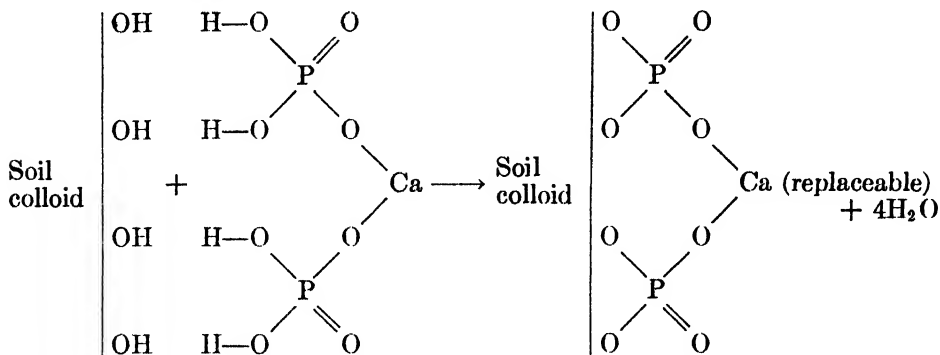
acid and alkaline samples. The 1.62 mmols of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ showed only slightly more effect than the 1.08 mmols.

Effect of phosphate

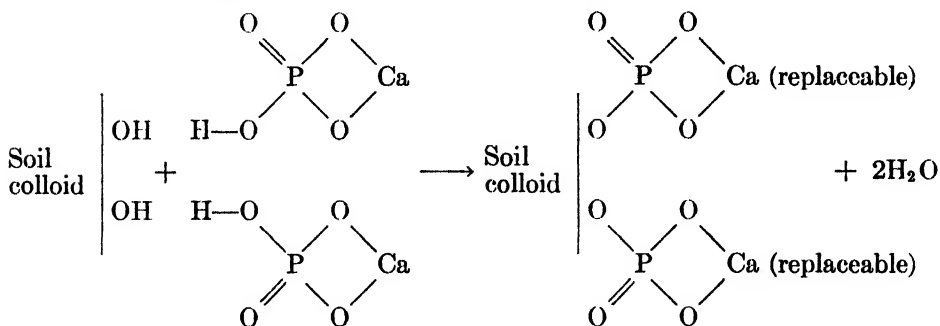
The data in table 1 show that monocalcium phosphate increased the cation-exchange capacity and the pH of the soil. These concurrent increases in exchange capacity and soil reactions, however, did not produce a significant change in the relation between base-exchange capacity and pH within the range of reaction commonly found in acid humid soils. This is shown by the curves in figure 1. As shown in figure 2 the magnitude of the increase in cation-exchange capacity shows two fairly definite points of change. The relationship of these changes in exchange capacity to other pertinent data are shown in table 5.

It will be seen from table 5 that the higher the pH value of the soil the larger is the increase in cation-exchange capacity produced by monocalcium phosphate. Furthermore, the magnitude of this increase in exchange capacity falls in three rather definite groups. Since the change in soil reaction within each series was obtained by additions of $\text{Ca}(\text{OH})_2$, it is suggested that the fixation of the phosphate and the increase in cation-exchange capacity can be represented by the following equations:

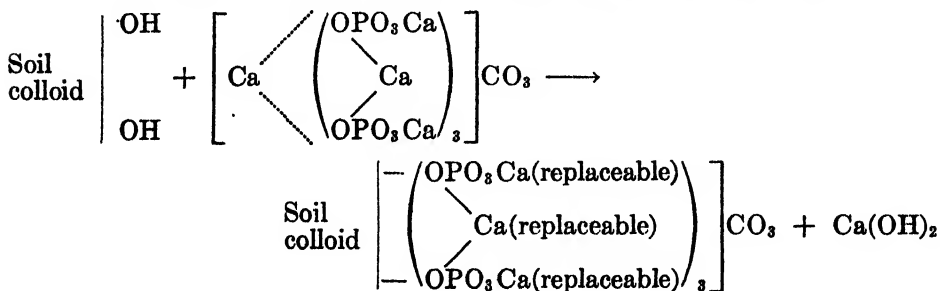
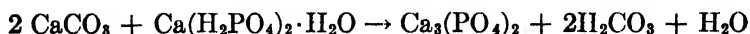
(1) For the range in pH at which $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is formed:



(2) For the range in pH at which $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is formed:



(3) For the pH range at which $\text{Ca}_3(\text{PO}_4)_2$ is formed (excess calcium or free CaCO_3)

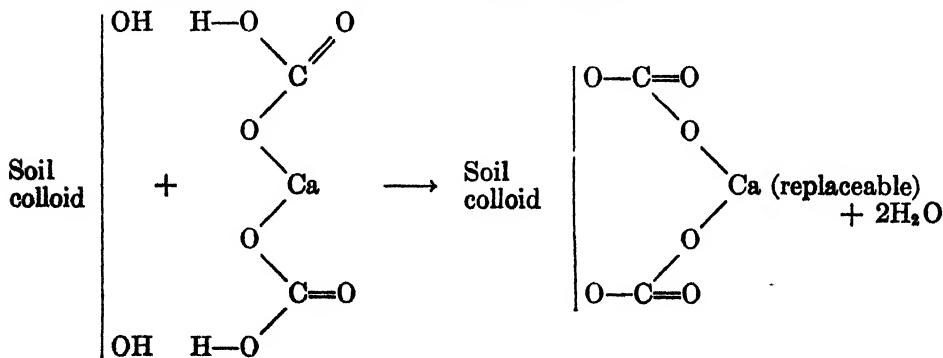


The pH values of the phosphate-treated series, given in table 5 (last column), at which the changes of calcium orthophosphate from monocalcium to dicalcium and from the dicalcium to the tricalcium forms occur are higher than the known values for aqueous solutions as indicated by Naftel's (26) data. The pH values in table 5 were obtained with 1:5 suspensions of soil in distilled H_2O . According to Donnan's law for equilibrium in colloidal systems the hydrogen-ion concentration in the micellar solution, where the chemical reactions took place, would be larger than that of the external solution. Consequently the pH values at which the reactions occurred would be smaller than the experimental values recorded. A clear exposition of the application of Donnan equations to H-ion concentrations in soils has been given by Mattson (23).

DISCUSSION

The literature on the subject and the data obtained indicate that air-drying soils may convert a part of the replaceable hydrogen or potassium into a non-replaceable form with a consequent decrease in the measurable exchange capacity. These changes are relatively small in magnitude but appear to be largest on acid soils that are high in exchangeable hydrogen and on soils that are saturated with bases or that contain free $CaCO_3$.

Large changes in pH value and cation-exchange capacity resulted from the treatment of the soils with $Ca(OH)_2$ and equilibration with CO_2 and air. In 1929 Parker (27) suggested the possibility that the treatment of soil with $Ba(OH)_2$ may further increase its exchange capacity, and Pierre and Scarseth (29) in 1930 found "that liming, like treating a soil with an alkaline solution, results in a build-up or the formation of additional exchange complex." It should be noted that the alkaline solution used was $Ba(OH)_2$. Under the conditions of the experiments reported herein, the "build-up" in cation-exchange capacity could not be due to the formation of basic salts, since these would not be stable at the reactions produced by treatment with carbonated water. Since this build-up in cation-exchange capacity occurred in the series in which each sample was carbonated immediately upon addition of the soil, it is suggested that this increase in exchange capacity is the result of the reaction of the soil with $Ca(HCO_3)_2$ as shown by the following equation:



The possibility that this reaction occurs in the soil is suggested by the data and the curves in figure 1 which show that the observed increases in cation-exchange capacity are related to the hydroxyl-ion concentration.

Though the combination represented by the foregoing equation could have occurred under the conditions of these experiments, it would be expected to be very unstable under the normal weathering influences of field conditions. The data reported by Muhr, Smith, and Weldon (25) on soil fertility plots showed only a small and statistically insignificant increase in exchange capacity as the result of regular biennial applications of lime for a period of 16 years. The increase in exchange capacity resulting from liming reported by Pierre and Scarseth (29) was obtained on soils in pot cultures in the greenhouse and not subjected to leaching.

It was pointed out in presenting the data that the additions of ferric and aluminum chloride decreased the measurable cation-exchange capacity of the soil. Furthermore, the magnitude of this decrease was more nearly comparable to the amount of calcium held by the probable forms of the orthophosphate formed at reactions below pH 7.2 than it was to the actual milliequivalents of Fe and Al added. In an earlier paper (7) the data presented on the increase in H_2O -soluble Ca produced by the additions of $FeCl_3 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ indicated that from 78 to 92 per cent of the Fe and Al added replaced Ca in the exchange complex of the soil. The reduction in cation-exchange capacity resulting from added iron and aluminum chlorides was less than 40 per cent of the milliequivalents of Fe and Al added in all but 3 of the 59 samples. Apparently the Fe and Al entered both the original base-exchange positions of the soil and those created by the addition of phosphate. In the former position they are replaceable, but in the latter they are not, i.e., the phosphate bonds holding Fe and Al ions are not broken by the chemical methods used for measuring cation-exchange capacity.

The fixation of phosphates by stoichiometric chemical reactions with the colloidal complex of soils has been discussed by several investigators. This form of fixation has been designated by some workers (18, 36) as an anionic exchange of the hydroxyl ion with the phosphate ion. Stout (34) showed that the relative abilities of kaolinite, halloysite, and bentonite to fix phosphate depended upon the presence in the clay mineral of hydroxyl ions which are available for exchange, or reaction, with the phosphate ion. The possible effect on cation-exchange properties which accompanies the chemical fixation of phosphates by soil colloids has been considered by Mattson and Hester (24) and Toth (36, 37).

Scarseth (31) believed that the phosphates retained by a natural aluminosilicate (bentonite) colloid at pH values of 5.5 to 6.1 were "sorbed on the colloidal surfaces of the aluminosilicate by the aluminum valence." He found the phosphate ion to be exchangeable and obtained replacement by the OH and SiO_4 anions. As an explanation of the larger amounts of phosphates retained by the Ca-series than by the Na-series—especially at alkaline reactions and

when large quantities of H_3PO_4 were added—he suggested a soil micelle-Ca-phosphate linkage. In a similar approach to the problem, Allison (2) studied the retention of phosphates by colloids from certain soils over a reaction range of pH 3.0 to 8.0. He found characteristic peaks of absorption (i.e., not water-soluble) at pH of 3.0 to 3.5 and at pH of 5.5 to 6.5. He considered the former to be due mainly to the hydrated forms of iron and the latter to aluminosilicate clay minerals and anion absorption. He also found that exchangeable calcium was indicated to be a factor in the retention of appreciable amounts of phosphates which were loosely held by a micelle-Ca- H_2PO_4 linkage.

The data given in tables 1 and 5 indicate that the phosphate may react with the soil as either the $[\text{CaPO}_4^-]$ or the $[\text{Ca}(\text{PO}_4)_2^{--}]$ and that the form is determined by the soil reaction. Furthermore, the form in which the phosphate is held by the soil, i.e., as the monocalcium or the dicalcium, appears to affect its availability to plants as indicated by its solubility in CO_2 -aspirated water (7).

Though no one manner of retention of phosphates by soils precludes the existence of other forms of retention in the same soil sample, the question arises as to whether applications of phosphate contribute materially to the improvement of soil fertility by regenerating or building up the cation-holding complex of the soil colloids. This phase of the problem of phosphate fixation seems to be at least worthy of further investigation.

SUMMARY

The cation exchange properties of a number of soil samples that had been brought to equilibrium in soil- H_2O - $\text{Ca}(\text{OH})_2$ - CO_2 -air systems were studied. Data concerning the effect of additions of monocalcium phosphate and of ferric and aluminum chloride upon the cation-exchange capacity and reaction of the soil in this system are given. These data may be summarized as follows:

Thorough air-drying of soil samples reduced the exchangeable hydrogen and cation exchange capacity of acid soils having a low degree of base saturation.

Liming soils with $\text{Ca}(\text{OH})_2$ or $\text{Ca}(\text{HCO}_3)_2$ under laboratory conditions produced an increase of the measurable cation-exchange capacity. This increase was separate and independent of the increased adsorption of polyvalent cations by soils which results from the formation of basic salts with the weak colloidal acids.

Phosphates react chemically with the basic constituents of soils. This reaction may be characterized as an anionic replacement of the hydroxyl ions with phosphate ions.

The change in cation-exchange capacity produced by liming was relatively large and increased in direct relationship to the hydroxyl-ion concentration. The increase in cation-exchange capacity resulting from the addition of monocalcium phosphate was relatively small and was dependent upon the amount of phosphate added.

The chemical reaction of phosphates with the soil complex results in strongly associated ions which increase the base-exchange complex and modify the pH value of the soil. Whether the orthophosphate is combined by the soil as the monocalcium or dicalcium form, or is precipitated as tricalcium phosphate, depends upon the pH at which the reaction occurs.

The addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ to the H_2O - $\text{Ca}(\text{OH})_2$ -soil systems decreased the cation-exchange capacity and increased the soil acidity of all samples. The concurrent changes in exchange capacity and pH value of the soil produced by additions

of monocalcium phosphate and iron and aluminum chloride resulted in little or no change, at reactions below pH 7.2, in the relationship between base-exchange capacity and soil reaction of the several series.

In the series in which the amount of Fe and Al added was equivalent to the added phosphate, the effect of the iron and aluminum upon cation exchange capacity approximately offset the effect of the phosphate in those samples having a soil reaction below pH 7.3.

It is suggested that the exchangeability of the cations that are held by the free bonds of the fixed phosphate depends upon the strength of the bonds as determined by the nature of the cation, e.g., calcium can be replaced but Fe and Al are not.

REFERENCES

- (1) ABEL, F. A. E., AND MAGISTAD, O. C. 1935 Conversion of soil potash from the non-replaceable to the replaceable form. *Jour. Amer. Soc. Agron.* 27: 437-445.
- (2) ALLISON, L. E. 1943 The trend of phosphate absorption by inorganic colloids from certain Indiana soils. *Soil Sci.* 55: 333-342.
- (3) BELL, A. P., AND THORNTON, S. F. 1937 The effect of season and fertilization on results of rapid chemical tests. *Soil Sci. Soc. Amer. Proc.* 2: 167-172.
- (4) BOWER, C. A., AND TRUOG, E. 1940 Base exchange capacity determinations as influenced by the nature of the cation employed and formation of basic salts. *Soil Sci. Soc. Amer. Proc.* 5: 86-89.
- (5) BRADFIELD, R., AND ALLISON, W. B. 1933 Criteria of base saturation in soils. *Trans. Second Comn. and Alkali Subcomn. Internatl. Soc. Soil Sci.* A: 63-79.
- (6) CONREY, G. W., AND SCHOLLENBERGER, C. H. 1927 The effect of weathering on exchangeable bases as shown in the Clermont silt loam profile. *Proc. First Internatl. Cong. Soil Sci. Comn.* 2: 212-229.
- (7) DAVIS, F. L. 1943 Retention of phosphates by soils: I. Effect of additions of iron and aluminum chloride upon the retention of phosphorus by virgin Hammond very fine sandy loam. *Soil Sci.* 56: 457-478.
- (8) DAVIS, F. L. 1943 The rôle of iron and aluminum in the retention of phosphates by soils as indicated by the solubility of phosphorus. *Soil Sci. Soc. Amer. Proc.* 8: 167-170.
- (9) DETURK, E. E., WOOD, L. K., AND BRAY, R. H. 1943 Potash fixation in Corn Belt soils. *Soil Sci.* 55: 1-12.
- (10) FINE, L. O., BAILEY, T. A., AND TRUOG, E. 1940 Availability of fixed potassium as influenced by freezing and thawing. *Soil Sci. Soc. Amer. Proc.* 5: 183-186.
- (11) GAARDER, T. 1930 Die Bindung der Phosphorsäure in Erdboden. *Vestl. Forstl. Førskssta. Meddel.* 14.
- (12) GOLDEN, L. B., GAMMON, N., AND THOMAS, R. P. 1942 A comparison of methods of determining the exchangeable cations and the exchange capacity of Maryland soils. *Soil Sci. Soc. Amer. Proc.* 7: 154-161.
- (13) HENDRICKS, S. B., AND FRY, W. H. 1930 The results of x-ray and microscopic examinations of soil colloids. *Soil Sci.* 29: 457-479.
- (14) JACKSON, M. L., AND TRUOG, E. 1939 Influence of grinding soil minerals to near molecular size on their solubility and base exchange properties. *Soil Sci.* 4: 136-143.
- (15) JOFFE, J. S., AND KOLODNY, L. 1936 Fixation of potassium in soils. *Soil Sci. Soc. Amer. Proc.* 1: 187-192.
- (16) JOFFE, J. S., AND KOLODNY, L. 1938 The effect of alternate drying and wetting on the base-exchange complex with special reference to the behavior of the K-ion. *Soil Sci. Soc. Amer. Proc.* 3: 107-111.
- (17) JOFFE, J. S., AND LEVINE, A. K. 1939 The relation of potassium fixation to the exchange capacity of soils. *Soil Sci. Soc. Amer. Proc.* 4: 157-161.
- (18) KELLEY, J. B., AND MIDGLEY, A. R. 1943 Phosphate fixation—an exchange of phosphate and hydroxyl ions. *Soil Sci.* 55: 167-176.

- (19) KELLEY, W. P. 1926 A general discussion of base exchange in soils. *Jour. Amer. Soc. Agron.* 18: 450-458.
- (20) KELLEY, W. P. 1930 The agronomic significance of base exchange. *Jour. Amer. Soc. Agron.* 22: 977-985.
- (21) KELLEY, W. P., DORE, E. H., AND BROWN, S. M. 1931 The nature of the base exchange material of bentonite, soils, and zeolites as revealed by chemical investigations and x-ray analysis. *Soil Sci.* 31: 25-54.
- (22) KERR, H. W. 1928 The nature of base exchange and soil acidity. *Jour. Amer. Soc. Agron.* 20: 309-335.
- (23) MATTSO, S. 1931 The laws of soil colloidal behavior: V. Ion adsorption and exchange. *Soil Sci.* 31: 311-331.
- (24) MATTSO, S., AND HESTER, J. B. 1935 The laws of soil colloidal behavior: XV. The degradation and regeneration of the soil complex. *Soil Sci.* 39: 75-84.
- (25) MUHR, G. R., SMITH, H. W., AND WELDON, W. P. 1943 Influence of cropping, manure, and manure plus lime on exchange capacity, pH, oxidizable material, and nitrogen of a fine-textured soil in eastern Nebraska. *Jour. Amer. Soc. Agron.* 35: 107-113.
- (26) NAFTEL, J. A. 1936 Soil liming investigations: II. The influence of lime on the sorption and distribution of phosphorus in aqueous and soil colloidal systems. *Jour. Amer. Soc. Agron.* 28: 740-752.
- (27) PARKER, F. W. 1929 The determination of exchangeable hydrogen in soils. *Jour. Amer. Soc. Agron.* 21: 1030-1039.
- (28) PEECH, M., AND BRADFIELD, R. 1942 The effect of lime and magnesia on the soil potassium and on the absorption of potassium by plants. *Soil Sci.* 55: 37-48.
- (29) PIERRE, W. H., AND SCARSETH, G. D. 1931 Determination of percentage base saturation of soils and its value in different soils at definite pH values. *Soil Sci.* 31: 99-114.
- (30) RAVIKOVITCH, S. 1939 Influence of exchangeable cations on the availability of phosphate in soils. *Soil Sci.* 47: 357-366.
- (31) SCARSETH, G. D. 1935 The mechanism of phosphate retention by natural aluminosilicate colloids. *Jour. Amer. Soc. Agron.* 27: 596-616.
- (32) SCHOLLENBERGER, C. J. 1930 Determination of carbonates in soil. *Soil Sci.* 30: 307-324.
- (33) SHAW, W. M., AND MACINTIRE, W. H. 1936 The relationship between water-soluble, replaceable, and fixed fractions of potash additions to soils. *Soil Sci. Soc. Amer. Proc.* 1: 143-147.
- (34) STOUT, P. R. 1939 Alterations in the crystal structure of clay minerals as a result of phosphate fixation. *Soil Sci. Soc. Amer. Proc.* 4: 177-182.
- (35) TAM, R. K., AND MAGISTAD, O. C. 1936 Chemical changes during decomposition of pineapple trash under field conditions. *Soil Sci.* 41: 315-327.
- (36) TOTH, S. J. 1937 Anion adsorption by soil colloids in relation to changes in free iron oxides. *Soil Sci.* 44: 299-314.
- (37) TOTH, S. J. 1939 The effect of free iron oxide removal on some properties of soil colloids. *Soil Sci.* 48: 385-401.
- (38) VOLK, N. J. 1934 The fixation of potash in difficultly available forms in soils. *Soil Sci.* 37: 267-287.
- (39) WAY, J. F. 1850 On the power of soils to absorb manure. *Jour. Roy. Agr. Soc. England* 11: 313-379.
- (40) WAY, J. F. 1852 On the power of soils to absorb manure. *Jour. Roy. Agr. Soc. England* 13: 123-143.
- (41) WOOD, L. K. AND DETURK, E. E. 1940 The absorption of potassium in soils in non-replaceable forms. *Soil Sci. Soc. Amer. Proc.* 5: 152-161.
- (42) WORSHAM, W. E., AND STURGIS, M. B. 1941 Factors affecting the availability of potassium in soils of the lower Mississippi delta. *Soil Sci. Soc. Amer. Proc.* 6: 342-347.

THE COMPARATIVE EFFECTS OF A 50-50 MIXTURE OF 1:3 DICHLOROPROPENE AND 1:2 DICHLOROPROPANE (D-D MIXTURE) AND OF CHLOROPICRIN ON NITRIFICATION IN SOIL AND ON THE GROWTH OF THE PINEAPPLE PLANT¹

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Carter (3) in 1943 reported the use of a promising new soil amendment and disinfectant composed of a 50-50 mixture of 1-3 dichloropropene and 1-2 dichloropropane (called "D-D mixture" for short). Among the benefits derived from the use of this mixture in plant tests was the control of the root-knot nematode (*Heterodera marioni*) in heavily infested soil. Since then other investigators at this institute³ have verified the effectiveness of D-D as a nematocide. *Anomala* and *Adorctus* larvae infesting nursery stock in soil have also been shown to be susceptible to water solutions of D-D mixture (4).

Because early observations (3) of pineapple plants grown in the field in soil treated with D-D at 150 pounds per acre gave no evidence of benefit from the treatment until more than a year after application, it was thought that the action of this disinfectant was different from that of others, such as chloropicrin, steam, formaldehyde, and calcium cyanide. The early rapid growth of pineapple plants in soil treated with chloropicrin, resulting in a dark green, broad-leaved, soft, succulent type of plant, was shown to be related to the inhibition of nitrification of applied ammonium, which limited these plants to an ammonium nutrition (12). Since the difference in the time of response of pineapple plants to treatment with D-D and with chloropicrin is important, a comparative study of the nitrogen nutrition of pineapple plants grown in soil following treatment with these two disinfectants was undertaken.

METHODS

Preparation and fertilization of soil

The soil used was a reddish-brown laterite from an upland Hawaiian pineapple area. Analysis of this soil, on the dry basis, was as follows: 19 p.p.m. of ammonium, 2 p.p.m. of nitrate, 90 p.p.m. of replaceable K_2O , trace of easily soluble P, 4.85 per cent organic matter, and pH 4.2.

After removal from the field, the soil was passed through a $\frac{1}{4}$ -inch screen to remove large clods, pebbles, and pieces of organic matter. Measured amounts of soil were mixed with 11.5-6.5-5.0 fertilizer compounded from ammonium sulfate, superphosphate, and potassium sulfate. Calculations showed, on the

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³ Unpublished results.

dry soil basis, that 176 p.p.m. of N, 99 p.p.m. of P_2O_5 , and 77 p.p.m. of K_2O were added. Recoveries of 175 p.p.m. of N and 71 p.p.m. of replaceable K_2O were made. Very little easily soluble P was recovered because of the rapid fixation of this element.

One hundred large enamelware pots of 0.8 cubic foot capacity were used for growing the plants. Fifty pounds of soil was placed in each pot. Disinfection was carried out individually in these containers.

Disinfection of soil

Chloropierin and D-D in the different treatments were applied at the rates shown in table 1.

Both disinfectants were delivered 6 inches below the soil surface with a glass-tube-glass-rod arrangement. At the time of treatment the soil moisture content was 23.5 per cent. The determined moisture equivalent of this soil was 27.7 per cent, and the calculated wilting coefficient was 19.8 per cent. Following treatment the pots were covered with mulch paper of the asphalt-impregnated

TABLE 1
Amounts of chloropierin and D-D applied to soil

TREATMENT SYMBOL	DISINFECTANT	PER ACRE	PER PLANT*	PER CUBIC FT. OF SOIL
		<i>lbs.</i>	<i>gm.</i>	<i>cc.</i>
A	None (check)			
B	Chloropierin	200	5.675	4.96
C	Chloropierin	400	11.350	9.92
D	Crude D-D	200	5.675	6.99
E	Crude D-D	400	11.350	13.98

* On the basis of 16,000 plants per acre.

type used in pineapple culture (8). After 4 days the covers were removed and the treated soil was allowed to air for 4 days before planting.

Measurements and analyses of plants

Pineapple slips from a single Cayenne clone within the limits of 150 to 220 gm. were planted in the soil. One slip was planted to each pot, and each treatment included 20 replicates. Immediately after planting, tap water was added to the maximum water-holding capacity of the soil. [Care was taken to minimize leaching and prevent the loss of soil nutrients.]

At intervals during the experiment, plant analyses were made according to the procedure outlined by Nightingale (7). Physical measurements taken were rate of growth as indicated by elongation of index leaves, size of plant as shown by length and width of the longest leaves, and color of plant by approximation of the percentage of surface of leaves showing yellow-green (No. 1), olive-green (No. 2), and dark green (No. 3) color.

When the plants had attained sufficient size, chemical analyses were made on

the white basal tissue of representative leaves from the group of maximum length. Each sample consisted of 10 leaves from 10 plants. Methods adapted for pineapple tissue (7) were used in determinations, including the phenoldisulfonic acid method for nitrate (5).

At the conclusion of the experiment, further analyses of the different parts of the plant were made. Total nitrogen was determined by a modified Kjeldahl method (2) using reduced iron to include nitrate (10). Soluble nitrogen was extracted by filtering after homogenizing the tissue in a Waring Blendor mixer. Since Sideris *et al.* (11) have shown the green part of the pineapple leaf to contain negligible amounts of nitrate- and ammonium-nitrogen, the determination of nitrogen of the filtrate was taken as soluble organic nitrogen. Figures for insoluble organic nitrogen were obtained by difference. Total chlorophyll was determined with the Klett-Summerson photoelectric colorimeter after extraction in the Waring Blendor with 70 per cent acetone and transference of the pigment to ether (9).

Soil sampling and analyses

Uniform cores of soil were obtained with a soil sampling tube from the pots at regular intervals for analysis. Soil from five pots was combined to make one sample, and triplicate samples from each treatment were analyzed.

Ammonium was displaced by a 10 per cent solution of KCl and distilled after being made alkaline with MgO (6). Nitrate was extracted with distilled water and determined by the phenoldisulfonic acid method (5). Easily soluble phosphorus was determined by the Denigès colorimetric procedure (13), replaceable potassium by the permanganate titration of the sodium cobaltinitrite precipitate (14), and organic matter by the wet combustion method (1). Soil pH was determined with the glass electrode using a soil:water ratio of 1:1 (2).

RESULTS

Root development

Since the suppression or elimination of the pathogenic macroorganisms and microorganisms of the soil is possibly the main reason for the use of soil disinfectants, close examinations and measurements of root development were necessary for the evaluation of benefit to the plant from soil disinfection. The values presented in table 2 are averages of measurements of six plants in each treatment taken at 33 weeks of age.

Treatment of soil with either chloropicrin or D-D stimulated the development of pineapple roots, causing statistically significant increases in total length (treatments B, C, D, and E), diameter (treatments B and C), and total dry weight (treatments C and D). Whatever damage to the root systems may have been caused by pathogenic organisms in the untreated soil was not immediately noticeable from general examination, since lateral roots were as abundant in the check as in the treated soil and nematode galls were absent from all treatments. Although the measurements showed the root systems in the check treatment to be inferior, they were probably adequate, as they did not appear to be

the limiting factor in plant growth. It will be demonstrated later that the group of plants in treatment D with the largest root system (35.5 gm.) made no more top growth than the plants in check treatment A with a root system of only 19.6 gm. dry weight. Both treatments A and D were on a nearly comparable nitrogen nutrition. Plants in treatments B, C, and E made better top

TABLE 2

Root observations and measurements of pineapple plants after growth for 33 weeks in soil treated with D-D and chloropicrin

SOIL TREATMENT	TOTAL LENGTH	AVERAGE* DIAMETER	TOTAL DRY WT.	NUMBER OF WHITE ROOT TIPS	NUMBER OF LATERAL ROOTS	NUMBER OF NEMATODE GALLS
	cm.	mm.	gm.			
A	1,926	1.46	19.6	8	many	0
B	2,978	1.69	26.2	12	many	0
C	2,868	1.65	30.6	12	many	0
D	2,976	1.51	35.5	10	many	0
E	2,641	1.52	23.9	11	many	0
Difference for significance ($p = 0.05$)	511	0.15	7.9			
($p = 0.01$)	691	0.20	10.7			

* Measured 3 cm. from end of white root tip.

TABLE 3

Species of non-gall-forming parasitic and saprophytic nematodes in soil treated with chloropicrin and D-D

TREATMENT AND REPLICATE	PARASITIC				SAPROPHYTIC	
	<i>Pratylenchus pratensis</i>	<i>Rotylenchus erythrinae</i>	<i>Pratylenchus macrophallus</i>	<i>Rotylenchulus reniformis</i>	<i>Aphelenchoides parietinus</i>	<i>Cephalobus</i>
A-1	++	+	++	+	+	+
A-2	++	+	+++	+	+	+
B-1	++	0	+	+	+	+
B-2	0	0	0	0	0	+
C-1	0	0	0	0	0	+
C-2	0	0	0	0	0	0
D-1	0	0	0	0	0	0
D-2	0	0	0	0	0	+
E-1	0	0	0	0	0	+
E-2	0	0	0	0	0	+

Ratings: 0 = none, + = present, ++ = numerous, +++ = abundant.

growth than those in treatment A, not because of better root systems, but because of an altered nitrogen nutrition.

It was noted that the roots in the chloropicrin treatments were thicker than those in the check and D-D treatments. They were also more succulent, since for nearly equal total lengths and greater diameter the total dry weights of the

roots in the chloropicrin treatments were smaller than those of the D-D treated plants of treatment D.

Although the plants in all the treatments were free from nematode galls, further tests⁴ showed the presence of several species of parasitic nematodes. Duplicate samples of roots from each treatment were laid out in shallow water in enamel pans. After 1 and 3 days the water was poured into glasses and allowed to stand. Samples from the bottom of the suspensions were examined qualitatively for nematodes with the results shown in table 3.

All the species of nematodes identified in the examination were found on the roots in treatment A (check). These undoubtedly contributed to the relatively small root systems found in that treatment, but how much the presence of these parasitic nematodes affected plant growth is problematical. It has been mentioned that top growth was not correlated with root volume in this experiment but was related to nitrogen nutrition.

Representatives of several species of parasitic nematodes in one replicate of treatment B may have survived the fumigation by 200 pounds chloropicrin. There were no parasitic nematodes in the 400-pound chloropicrin (C), 200-pound D-D (D), and 400-pound D-D (E) treatments but only the saprophytic cephalobids, which were probably chance contaminants introduced after fumigation.

Soil nitrogen

Ammonium nitrogen added in the form of ammonium sulfate at the rate of 176 p.p.m. on the dry soil basis was rapidly nitrified in the untreated soil of treatment A (figs. 1 and 2). Nitrate in this soil increased from 9 p.p.m. at the beginning to 78 p.p.m. at 24 weeks, a net gain of 69 p.p.m., disregarding the amount absorbed by the plant. Ammonium, on the contrary, decreased from 170 p.p.m. to 35 p.p.m., for a total loss of 135 p.p.m.

Ammonium nitrogen in the soil treated with 200 pounds of D-D (treatment D) remained in that state for at least 8 weeks. Sometime between 8 and 13 weeks after disinfection, nitrification was resumed in this experiment, nitrate increasing from 5 p.p.m. to 31 p.p.m. in the 5-week interval. Resumption in nitrification occurred about the time the pineapple plants became well established and began to absorb nutrients in appreciable amounts from the soil. A total of 91 p.p.m. of available nitrogen was lost or taken up by plants in this treatment. This amount was slightly more than that of treatment A.

The application of 200 pounds of chloropicrin (treatment B), 400 pounds of chloropicrin (treatment C), and 400 pounds of D-D (treatment E) suppressed nitrification for 24 weeks. In all three treatments nitrate varied from 7 or 8 p.p.m. to traces during the experimental period. Nitrogen taken up from the soil by the plants in these treatments was mainly in the form of ammonium. The amounts lost from the soil were: B, 118 p.p.m., C, 105 p.p.m., and E, 109 p.p.m. These quantities exceeded the uptake in treatment A, which was classi-

⁴ The author is indebted to Juliette M. Oliveira for her assistance in the testing for and identification of species of nematodes.

fied mainly as nitrate nutrition, and in treatment D, which was rated as intermediate between ammonium and nitrate.

The maximum recovery of total available nitrogen in all the treatments was at either the 4- or the 6-week samplings. Only in treatment D did the amount of nitrogen recovered exceed that of the check treatment A. It was obvious that the applications of chloropicrin and D-D in this experiment could account for, at most, only negligible quantities of nitrogen added to the soil. Those amounts were too small to account for the increased absorption of nitrogen and plant growth in the disinfected soils. Amounts of nitrogen recovered after the 6- or 8-week samplings could not be taken as representative, since at this age plants became established and began to take up nitrogen in greater or smaller amounts depending on the form of nitrogen predominant in the soil.

Nitrate nitrogen of plants

Under normal conditions, the pineapple plant absorbs and stores appreciable amounts of nitrate in the white basal tissue of the leaves when nitrate is available in the soil. When the process of conversion of ammonium to nitrate in the soil is in some way inhibited, very little nitrate is found in the plant. Growth of the plant is not retarded, however, and experiments have shown (11) that the pineapple plant absorbs and assimilates ammonium more rapidly than nitrate. This results in a faster growing, larger, greener, and more succulent plant, provided carbohydrates are not a limiting factor.

Data presented in figures 1 and 2 show that the application of D-D and chloropicrin interfered with the conversion of added ammonium sulfate to nitrate in soil for varying lengths of time. This subjected the plants grown in treated and untreated soil to different degrees of nitrate or ammonium nutrition as indicated by the amounts of nitrate in the basal white leaf tissue from the time the plants were 18 to 35 weeks old, when the experiment was concluded (figs. 1 and 2).

Plants grown in untreated soil (treatment A) contained a high percentage of leaf nitrate early in their development. When 18 weeks old, plants in this treatment showed a leaf nitrate content of 0.082 per cent. Since analysis of the soil at 18 weeks indicated the presence of 53 p.p.m. of nitrate and 37 p.p.m. of ammonium, the nutrition of the plants in this treatment was classified as predominantly nitrate.

Plants grown in soil treated with 200 and 400 pounds chloropicrin contained only traces of leaf nitrate when 18 weeks old and the amounts at any time up to 35 weeks did not exceed 0.009 per cent. Treatment of the soil with chloropicrin limited these plants almost entirely to an ammonium nutrition.

Treatment of the soil with 200 pounds of D-D suppressed nitrification for only 8 weeks. This allowed the plants to receive a good portion of their nitrogen as nitrate despite disinfection. The proportion of nitrate to ammonium in the soil at 18 weeks was 39 p.p.m. to 62 p.p.m., and the leaf nitrate content was 0.066 per cent. The plants in this treatment (D) were classified as intermediate between nitrate and ammonium nutrition.

Although soil nitrate determinations did not show the presence of appreciable

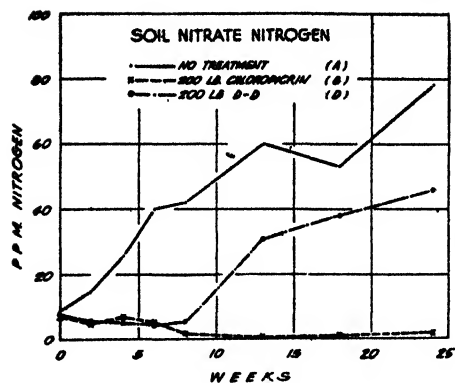


FIG. 1a. SOIL NITRATE NITROGEN IN TREATMENTS A, B, AND D

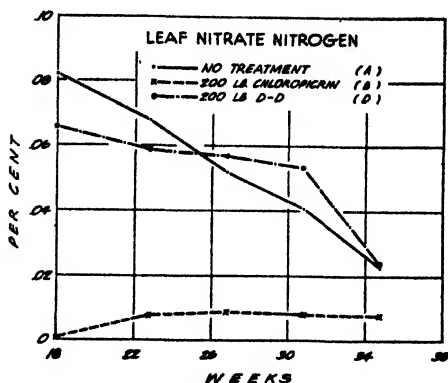


FIG. 1b. LEAF NITRATE NITROGEN IN TREATMENTS A, B, AND D

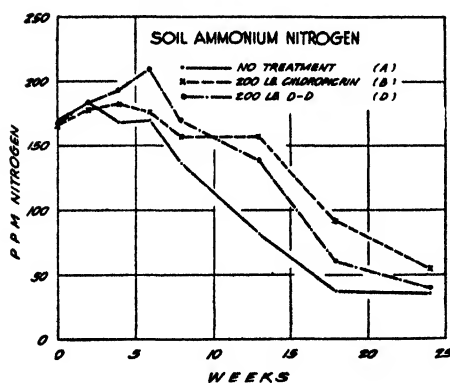


FIG. 1c. SOIL AMMONIUM NITROGEN IN TREATMENTS A, B, AND D

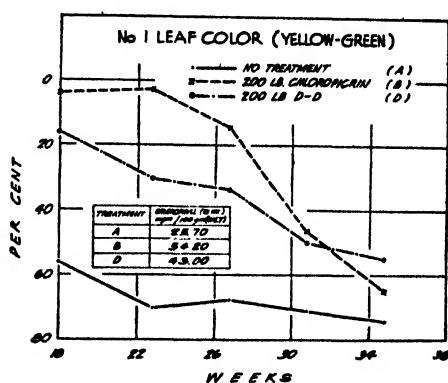


FIG. 1d. MEASUREMENTS OF No. 1 LEAF COLOR (YELLOW-GREEN) OF PINEAPPLE PLANTS IN TREATMENTS A, B, AND D

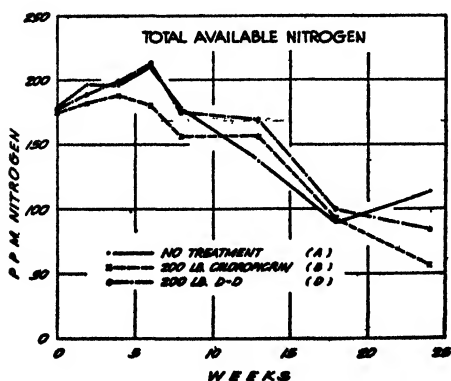


FIG. 1e. TOTAL AVAILABLE NITROGEN OF SOIL IN TREATMENTS A, B, AND D

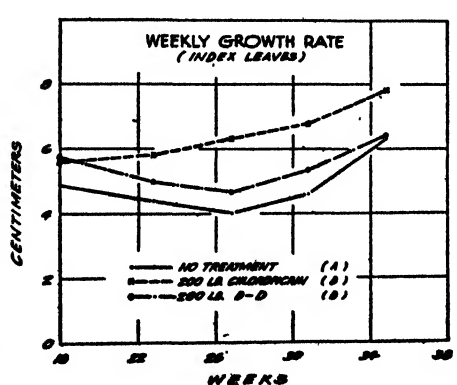


FIG. 1f. WEEKLY GROWTH RATES OF PINEAPPLE PLANTS IN TREATMENTS A, B, AND D (INDEX LEAVES)

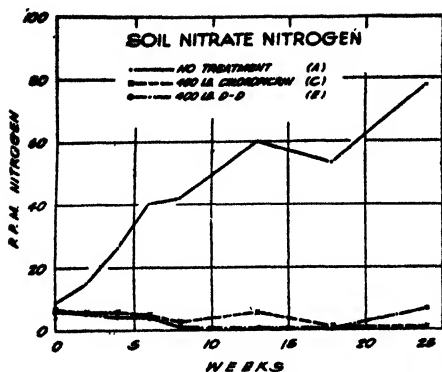


FIG. 2a. SOIL NITRATE NITROGEN IN TREATMENTS A, C, AND E

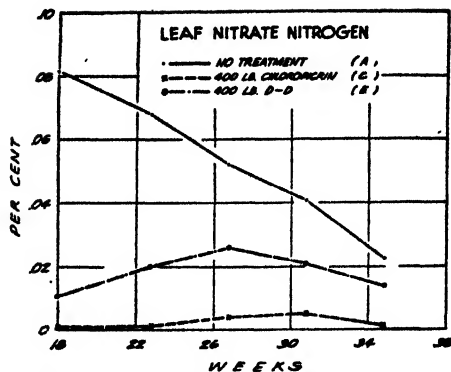


FIG. 2b. LEAF NITRATE NITROGEN IN TREATMENTS A, C, AND E

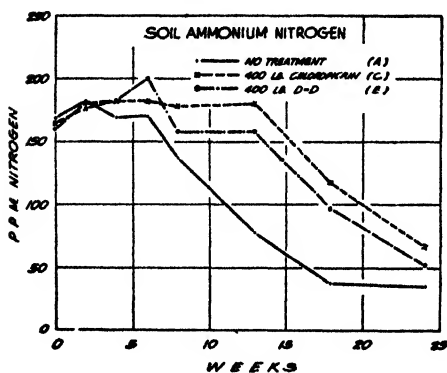


FIG. 2c. SOIL AMMONIUM NITROGEN IN TREATMENTS A, C, AND E

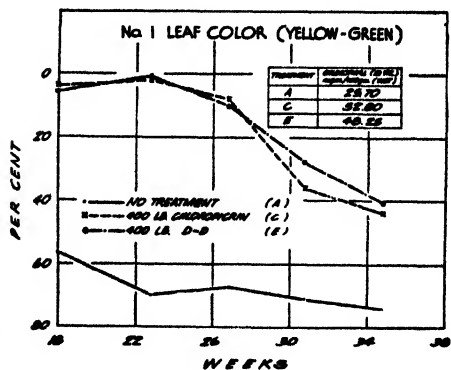


FIG. 2d. MEASUREMENTS OF No. 1 LEAF COLOR (YELLOW-GREEN) OF PINEAPPLE PLANTS IN TREATMENTS A, C, AND E

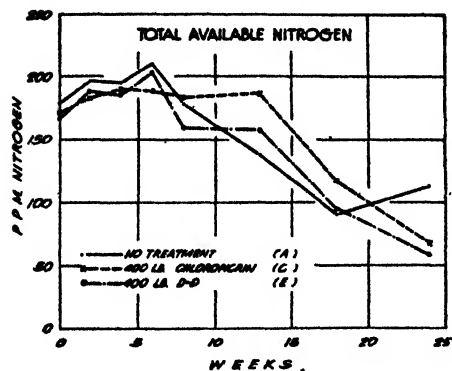


FIG. 2e. TOTAL AVAILABLE NITROGEN OF SOIL IN TREATMENTS A, C, AND E

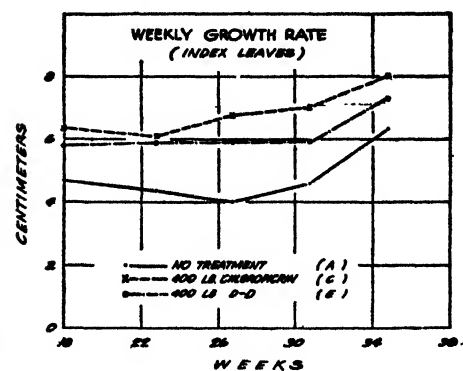


FIG. 2f. WEEKLY GROWTH RATES OF PINEAPPLE PLANTS IN TREATMENTS A, C, AND E (INDEX LEAVES)

amounts of nitrate in the soil treated with 400 pounds of D-D (treatment E), amounts of leaf nitrate of 0.011, 0.020, 0.026, 0.021, and 0.014 per cent between 18 and 35 weeks evidenced the absorption of small amounts of nitrate by these plants. This substantiates earlier observations which demonstrated leaf analysis to be a more sensitive index of nitrification in soil than soil nitrate determinations (12). The source of nitrogen, however, was chiefly ammonium.

Plant growth

The differences in plant growth resulting directly from either nitrate or ammonium nutrition and indirectly from soil disinfection were measured during the growth period of the plant. Figures 1 and 2 present data for No. 1 leaf color (yellow-green) and weekly growth rate.

Under normal field conditions without fumigation, No. 1 leaf color (indicating degree of yellowness of the plant) is inversely proportional to the amount of leaf nitrate. Hence, the normal practice is to invert the ordinate for No. 1 leaf color to match the curves for leaf nitrate and No. 1 leaf color. When soils are disinfected, however, No. 1 leaf color is directly related to amounts of leaf nitrate. Thus, low leaf nitrate (high ammonium) results in low No. 1 leaf color (greener plant). This relationship was shown to be true with plants grown in soil treated with either chloropicrin or D-D. Values for chlorophyll determinations made at 18 weeks, also presented in figures 1 and 2, substantiate visual readings made for No. 1 leaf color.

The weekly rate of growth as evidenced by index leaf measurements was lowest in the check, high-nitrate plants (treatment A). The highest rates of growth were in the chloropicrin-treated plants, which were almost entirely on an ammonium nutrition (treatments B and C). The rate of growth for the plants treated with 200 pounds D-D (treatment D) was higher than that of the check treatment but lower than that of the plants with 200 pounds of chloropicrin. The plants in the 400 pounds D-D treatment (E) grew faster than plants with 200 pounds D-D. Rate of growth of plants was related to ammonium and not to nitrate in the soil.

At the end of the growth period of 35 weeks, representative plants from each treatment were harvested, and the different parts of the plants were weighed and measured. These expressions of vegetative development are presented in table 4.

The largest amounts of dry matter (treatment B, 184.4 gm.; treatment C, 185.5 gm.) were elaborated by the chloropicrin-treated plants, which were almost entirely on an ammonium nutrition during the 35-week growth period. This is in contrast to the low amounts for the check treatment A (138.4 gm.) and the 200 pounds D-D treatment D (148.0 gm.), in both of which treatments plants absorbed considerable amounts of nitrate during the growth period. With further restriction in nitrate supply, the plants in the 400 pounds D-D treatment (E) yielded a higher amount of dry matter (163.6 gm.). Increases above the check in treatments B, C, and E were statistically significant.

The greatest increases in dry matter in the treated plants were in the leaves. Although the total dry matter in the stems of the check treatment was higher

than that of the other treatments, the differences were not significant. The percentage dry matter of the stems of the check plants was significantly greater, however, than that of the treated plants, indicating less succulence and possibly greater carbohydrate storage in the former. The same trend was also noted in the leaves, but possibly because of the small number of replicates, the differences were not significant.

Plants in the chloropicrin treatments (B and C) and the high D-D treatment (E) had a significantly larger number of leaves over 12 inches long than those of the check treatment (A). The difference between these treatments in the size of the leaves as shown by the length and width of the longest leaf was also found to be statistically significant. These differences in the quantity and quality of plant growth were probably due to contrasting nitrate and ammonium nutrition caused by soil disinfection.

TABLE 4

Amounts of dry matter and measurements of plants grown for 35 weeks in soil treated with chloropicrin and D-D

TREATMENT	DRY MATTER PER PLANT				PERCENTAGE DRY MATTER		NUMBER OF LEAVES OVER 12 INCHES	LONGEST LEAF	
	Leaves	Stem	Total top	Total top + roots	Leaves	Stem		Length	Width
	gm.	gm.	gm.	gm.				cm.	cm.
A	107.6	11.2	118.8	138.4	16.13	17.87	24.0	57.5	6.07
B	148.8	9.4	158.2	184.4	15.43	14.37	27.2	70.8	6.37
C	146.3	8.6	154.9	185.5	15.58	14.43	26.3	72.5	6.57
D	104.3	8.2	112.5	148.0	15.53	15.40	23.2	63.3	6.07
E	130.7	9.0	139.7	163.6	14.99	14.33	26.0	70.0	6.18
Difference for significance									
($p = 0.05$)	19.92	4.74	20.46	18.94	2.926	2.437	2.0	5.2	0.32
($p = 0.01$)	28.33	7.85	29.11	26.93	4.853	3.467	2.7	7.0	0.44

Total absorption of nitrogen

When the plants were 33 weeks old, three plants in each treatment were selected at random and divided into several parts. Weights for each section were recorded and total nitrogen was determined after drying of the tissues. The total amount of nitrogen in each plant part was calculated and is presented in table 5.

The average of 1,564 mgm. of nitrogen taken up by plants in the check treatment (A) was the smallest amount for any of the treatments. Increases over the check of 1026 and 1023 mgm. nitrogen in treatments B and C are attributed primarily to soil disinfection by chloropicrin and subsequently to the limitation of the plants to an ammonium nutrition. In the plants grown in soil treated with 400 pounds D-D (treatment E), in which small amounts of nitrate were found in the basal white leaf tissue, the gain in nitrogen in the plant (786 mgm.) was less than that for the chloropicrin plants, which contained only negligible

amounts of nitrate during the growth period. In the 200 pounds D-D treatment (D), where plants absorbed considerable amounts of nitrate, the amount of nitrogen absorbed above that of the check was only 328 mgm. per plant. This amount, however, was still above the 244 mgm. necessary for statistical significance (odds 19 to 1). It is evident that the increased amounts of nitrogen absorbed by the plants in each disinfection treatment were directly related to the amounts of ammonium available in the soil, and inversely related to the amounts of nitrate in the soil and in the white basal tissue of the leaves.

Distribution of nitrogen in the plant

When 27 weeks old, three plants from each treatment were harvested and nitrogen determinations were made on various parts of the leaves. A limited separa-

TABLE 5

Total nitrogen in different parts of the pineapple plant treated with chloropicrin and D-D

PART OF PLANT*	TOTAL NITROGEN WITH SOIL TREATMENT				
	A	B	C	D	E
	mgm.	mgm.	mgm.	mgm.	mgm.
A & B leaves (white and green tissue)	340	623	592	430	556
C & D leaves (white tissue)	136	142	119	102	121
C & D leaves (green tissue)	660	1269	1298	886	1046
E & F leaves (white tissue)	82	100	103	76	111
E & F leaves (green tissue)	153	273	309	202	323
Stem	193	183	166	196	193
Total per plant†	1564	2590	2587	1892	2350
Amount above treatment A		1026	1023	328	786
Percentage above treatment A		65.6	65.4	21.0	50.3

* Cf. classification to plant parts, Sideris *et al.* (11).

† Difference between totals necessary for significance ($p = 0.05$) 244 ($p = 0.01$) 347.

tion of the total nitrogen into soluble organic and insoluble organic fractions was made on the basal, medial, and distal one-third sections of the green tissue of the "D" group of leaves of maximum length. The results are presented in figure 3.

Soluble organic nitrogen in the basal section of the green tissue of "D" leaves in treatments A (check) and D (200 pounds D-D) on nitrate nutrition was higher than for treatments B (200 pounds chloropicrin), C (400 pounds chloropicrin), and E (400 pounds D-D) on ammonium nutrition. In the distal part of the leaf, the percentages of soluble organic nitrogen in treatments B, C, D, and E were much higher than that of treatment A. Hence, there appears to be a greater translocation and concentration of soluble organic nitrogen in the distal parts of the leaves of plants subjected to ammonium nutrition than in those on nitrate nutrition. From the results of more extensive studies by Sideris

et al. (11), the concentration of soluble organic nitrogen in the distal section of leaves of pineapple plants grown in ammonium solutions may be attributed either to greater translocation of the organic nitrogen compounds formed in the plant from ammonium or to a larger amount of nitrogen which was absorbed and assimilated at the time the tissues were formed.

Since treatments A and D were on a somewhat similar nitrate and partial nitrate nutrition, the distribution of insoluble nitrogen in the leaves of both treatments was similar. The highest concentration was in the medial section with comparatively high amounts in both the basal and distal sections. The distribution in treatments B, C, and E (ammonium nutrition) was of a different pattern. A small percentage was found in the basal section, a higher concentration in the medial section, and the highest concentration was in the distal

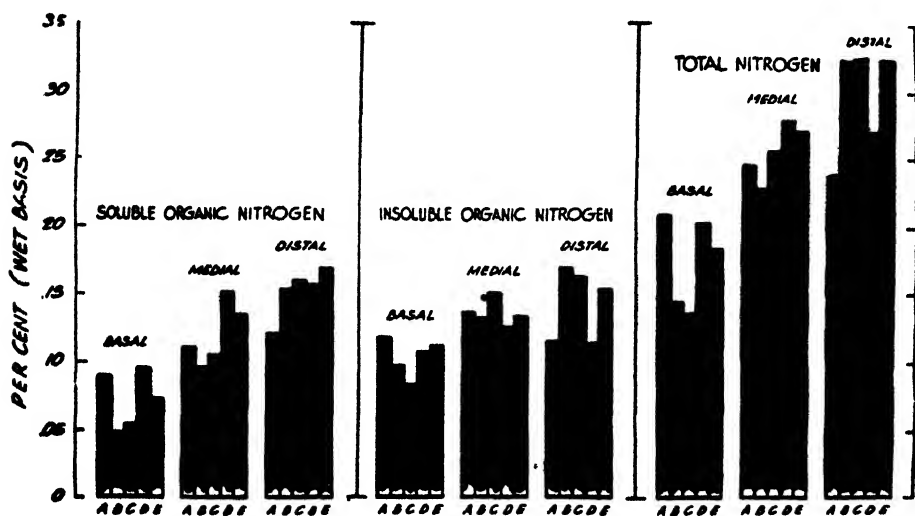


FIG. 3. DISTRIBUTION OF NITROGEN IN DIFFERENT PARTS OF THE GREEN TISSUE OF "D" LEAVES OF PINEAPPLE PLANTS GROWN IN UNTREATED AND IN CHLOROPICRIN AND D-D-TREATED SOILS

section of the leaves. The distribution of total nitrogen in all the treatments followed the patterns described for insoluble nitrogen.

DISCUSSION

Possibly the greatest benefit to the plant from soil disinfection is the elimination of harmful organisms from the soil or at least the disturbance of the balance of organisms to the extent that the pathogenicity of the parasites is reduced. The observation (3) that pineapple plants grown in certain soils treated with 150 pounds per acre of D-D did not show better growth until a full year after planting can well be related to this known effect of soil disinfection. It has been noted (3) and verified in this experiment that D-D is a very efficient nematicide.

Besides the effect of disinfectants on parasites, it has been pointed out in an earlier paper (12) that in soil where pathogenic organisms are not of major im-

portance the disturbance of the rate of nitrification of added ammonium to the soil is equally important to the growth of plants. Pineapple plants restricted to an ammonium nutrition showed an early rapid growth characterized by dark green color, broad leaves, high nitrogen, softness, and succulence. This has often been observed with chloropicrin under field conditions with some soils.

The results presented in this report indicate that, with equal amounts of D-D and chloropicrin under similar conditions, D-D does not suppress nitrification in soil so efficiently as does chloropicrin. The application of D-D at the rate of 200 pounds per acre prevented nitrification for only a little over 8 weeks. The same application of chloropicrin was effective for at least 24 weeks. The application of 400 pounds of D-D, however, resulted in very little nitrate formation in the same soil.

Plant growth as measured by the formation of total dry matter was related to the length of time the plants were on an ammonium nutrition. The least growth was made by plants in the check treatment where comparatively large amounts of both soil and leaf nitrate were found. Plants treated with 200 pounds D-D, in which nitrate was available after 8 weeks, showed only a negligible gain in total dry matter but an appreciable gain in total absorbed nitrogen. The largest amounts of absorbed nitrogen and of total plant growth were in the treatments in which nitrification was totally or nearly completely suppressed for 24 weeks. These were the treatments with 200 and 400 pounds chloropicrin and 400 pounds D-D. Hence, rate of growth, quality of growth, total elaboration of organic matter, and total absorption of nitrogen were related to type of nitrogen nutrition in this experiment.

Size and rate of growth of the tops of the plants were not related to the volume or weight of roots. Although treatment with 200 pounds of D-D produced the largest root system, the top growth of these plants was no greater than that of the checks with the smallest root system.

It cannot be emphasized too strongly that the comparative results obtained from the amounts of D-D and chloropicrin used in this experiment may not be applicable under field conditions. Scarcely anything is known at present of the optimum conditions under which benefit may be derived from the use of D-D. It is possible that, with different soils and under varying degrees of soil porosity, moisture, pH, and methods of application and confinement of the gas, D-D in smaller amounts may be equally beneficial or even superior to chloropicrin in promoting plant growth. The present experiment merely indicates one of the ways in which D-D may stimulate plant growth.

The results of this experiment suggest that under certain conditions the use of high enough amounts of D-D will suppress nitrification of ammonium in soil. If this were brought about, early rapid growth of pineapple plants characterized by dark green color, broad leaves, softness, and high nitrogen content would result. In this respect, D-D would not be different from chloropicrin in determining plant growth by affecting soil nitrification of added ammonium sulfate. That D-D in some cases fails to improve the appearance of plants until a year or more after disinfection may be related primarily to the destruction of pathogenic

organisms in soil, which allow the treated plants to maintain an actively functioning, healthy root system at maturity. Plants in untreated soil may be extensively attacked at this age by root pathogens, as observed in many pineapple-producing areas. The inferiority of D-D mixture to chloropicrin in suppressing nitrification should be presently considered subordinate to its known efficiency against certain plant pathogenic organisms in soil. The milder effect of D-D on nitrifying organisms may be desirable with many crops which apparently do better with nitrate nutrition under certain conditions.

SUMMARY

A comparative study was made of the effect of D-D mixture (a 50-50 mixture of 1-3 dichloropropene and 1-2 dichloropropane) and of chloropicrin on the process of biological nitrification in soil and its subsequent effects on ammonium and nitrate absorption, root development, rate of growth, quality of growth, and total elaboration of organic matter by the pineapple plant. Since plants with the largest root systems made no more growth than plants with the smallest volume of roots on nearly similar nitrate nutrition, it was considered that amount of top growth and total nitrogen absorption were related to the ammonium supply in the soil and, hence, to the suppression of nitrification by the disinfectants.

Under the conditions of the present experiment, it was found that 200 pounds D-D suppressed nitrification for 8 weeks and 200 pounds chloropicrin was inhibitory for at least 24 weeks. The application of 400 pounds D-D was more effective than 200 pounds D-D, but not so efficient as 200 pounds of chloropicrin. In every case, leaf nitrate of the pineapple plant correlated with the amount of nitrate found in the soil.

The total amount of nitrogen absorbed by the plants at the completion of a growth period of 35 weeks was lowest in the check treatment, which was on a high-nitrate nutrition. An appreciable increase in absorbed nitrogen was found in the 200-pound D-D treatment, which was on a partial nitrate and ammonium nutrition. The highest amounts of total nitrogen were in the plants on a nearly complete ammonium nutrition; namely, 400-pound D-D, 200-pound chloropicrin, and 400-pound chloropicrin treatments.

Plants in the check and in the 200-pound D-D treatment which were supplied with appreciable amounts of nitrate during the growth period were slower-growing, yellower (higher No. 1 yellow-green leaf color and lower concentration of chlorophyll), higher in percentage dry matter, lower in total dry matter, and absorbed smaller amounts of available soil nitrogen than plants in the other treatments. The plants growing in soil treated with 400 pounds D-D, 200 pounds chloropicrin, and 400 pounds chloropicrin were restricted to ammonium as a source of nitrogen and were characterized as a high-nitrogen, dark green (low No. 1 yellow-green color and high chlorophyll content), fast-growing (high total dry matter), broad-leaved, soft, and succulent (low percentage dry matter) type.

Although no nematode galls were formed on the root systems of the plants in any of the treatments, examinations for non-gall-forming nematodes indicated

D-D to be a more efficient nematicide than chloropicrin. It was suggested that delayed response of pineapple plants to D-D may be related to improved root systems at maturity due to control of root pathogens by the disinfectant. The use of sufficiently high concentrations of D-D to inhibit nitrification in soil will be evidenced by early response resulting in the typical ammonium plants seen after chloropicrin treatment of soil.

REFERENCES

- (1) Association of Official Agricultural Chemists 1935 Official and Tentative Methods of Analysis, ed. 4. Washington, D. C.
- (2) Association of Official Agricultural Chemists 1940 Official and Tentative Methods of Analysis, ed. 5. Washington, D. C.
- (3) CARTER, W. 1943 A promising new soil amendment and disinfectant. *Science* (n.s.) 97: 383-384.
- (4) CARTER, W. 1944 The use of D-D mixture against *Anomala* and *Adoretus* infesting nursery stock. *Jour. Econ. Ent.* 37: 117-118.
- (5) HARPER, H. J. 1924 The accurate determination of nitrates in soils. *Indus. and Engin. Chem.* 16: 180-183.
- (6) HARPER, H. J. 1924 The determination of ammonia in soils. *Soil Sci.* 18: 409-418.
- (7) NIGHTINGALE, G. T. 1942 Nitrate and carbohydrate reserves in relation to nitrogen nutrition of pineapple. *Bot. Gaz.* 103: 409-456.
- (8) JOHNSON, M. O. 1935 The Pineapple. Honolulu, Hawaii.
- (9) PETERING, H. G., WOLMAN, W., AND HIBBARD, R. P. 1940 Determination of chlorophyll and carotene in plant tissue. *Indus and Engin. Chem., Analyt. Ed.* 12: 148-151.
- (10) PUCHER, G. W., LEAVENWORTH, C. S., AND VICKERY, H. B. 1930 Determination of total nitrogen of plant extracts in presence of nitrates. *Indus. and Engin. Chem., Analyt. Ed.* 2: 191-193.
- (11) SIDERIS, C. P., KRAUSS, B. H., AND YOUNG, H. Y. 1938 Assimilation of ammonium and nitrate by pineapple plants grown in nutrient solutions and its effects on nitrogenous and carbohydrate constituents. *Plant Physiol.* 13: 489-537.
- (12) TAM, R. K., AND CLARK, H. E. 1943 Effect of chloropicrin and other soil disinfectants on the nitrogen nutrition of the pineapple plant. *Soil Sci.* 56: 245-261.
- (13) TRUOG, E., AND MEYER, A. H. 1929 Improvements in the Denigès colorimetric method for phosphorus and arsenic. *Indus. and Engin. Chem., Analyt. Ed.* 1: 136-139.
- (14) VOLK, N. J., AND TRUOG, E. 1934 A rapid chemical method for determining the readily available potash of soil. *Jour. Amer. Soc. Agron.* 26: 537-546.

AVAILABILITY OF REPLACEABLE CALCIUM FROM DIFFERENT TYPES OF COLLOIDS AS AFFECTED BY DEGREE OF CALCIUM SATURATION¹

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The discovery that soil colloids are predominately composed of clay minerals has set in motion a number of researches on the chemical and physical properties of specimens of the several recognized types of such minerals. This investigation is concerned with the effect of the mineralogical and chemical nature of colloids on the availability to plants of replaceable calcium.

It has been demonstrated that replaceable cations are an important source of plant nutrients, and that plants obtain these nutrients by cation-exchange reactions. The influence of the nature of the soil colloid in these exchange reactions is not well understood, however, and it seems likely that quantitative measurements of this factor will aid in the laboratory evaluation of soil fertility. The object of this investigation was to compare the manner in which different types of colloids release their replaceable Ca to growing plants and to solutions of electrolytes, and to measure the effect of percentage Ca saturation of the various colloids upon the magnitude of this release.

REVIEW OF LITERATURE

Investigations of the availability to plants of the replaceable Ca of the soil have been recently reviewed by Pierre and Allaway (13). Several workers (2, 6, 7, 8, 12) have shown that the growth of plants on acid soils and the ability of these plants to absorb nutrient cations are enhanced by increasing the percentage base saturation. Some of the same workers have also shown that the nature of the other ions on the complex may exert a marked effect on the replaceability and plant availability of any replaceable cation.

Albrecht and his associates (1) have emphasized that the technique of growing soybeans in sand-colloid cultures can be very useful for investigating the various factors concerned with Ca availability. In the Putnam colloid used in their work the availability of Ca from Ca-H systems increased regularly with increases in the percentage Ca saturation.

One of the first to determine the replaceability of Ca from different types of clay minerals was Schachtschabel (14). He found that montmorillonite tended to hold Ca in preference to K or NH₄, whereas mica-like clays held K or NH₄ more tightly than Ca. Hendricks and Alexander (5) found, however, that the variation within certain types of clay minerals in respect to some of their cation-exchange characteristics was as great as the variation among different types. Nevertheless, certain cation-exchange properties were fairly characteristic of some mineralogical groups.

Marshall and his associates (9) have recently measured the activity of the replaceable cations in suspensions of various clay minerals by means of a mineral membrane electrode.

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Their results indicate that monovalent cations are more highly dissociated from kaolinite than from illite, Wyoming bentonite, or the Putnam colloid.

In the aforementioned review article it was pointed out that the availability of replaceable cations of different soils at a given degree of saturation probably varies with the nature of the colloids present. This factor was investigated by Elgabaly, Jenny, and Overstreet (3), who found that K and Zn were more readily available to barley roots from montmorillonite than from kaolinite, although kaolinite released greater amounts of these ions in equilibrium with electrolytes.

While this investigation was in progress, Mehlich and Colwell (10) offered evidence to show that Ca was more readily available to cotton and soybeans when held by kaolinitic or organic colloids than when held by a montmorillonitic soil colloid. The reverse was true of magnesium. The availability of both ions was related to their replaceability by one symmetry concentration of HCl.

MATERIALS

The following materials were selected as typical of certain clay mineral types known to occur in soils:

1. Illite—a fraction of equivalent diameter $< 2 \mu$ obtained from material supplied by Dr. R. E. Grim, of the Illinois Geological Survey. This material occurred at Goose Lake, Ill.
2. Wyoming bentonite—prepared from Kwicksol bentonite (American Colloid Co., Chicago, Ill.).
3. Kaolinite—Peerless No. 1 Clay from Bath, S. C. (R. T. Vanderbilt Co., New York City, N. Y.).
4. Mississippi bentonite—prepared from Panther Creek bentonite (American Colloid Co.). This material was mined at Aberdeen, Miss.

Since the last three samples were nearly all finer than 2μ , no size fractionation of them was practiced.

Thermal analyses of samples 1, 2, and 4 have been published by Grim and Rowland (4). These materials are considered to be good examples of the illite (no. 1) and the montmorillonite (nos. 2 and 4) groups of clay minerals. Thermal data for the kaolinite used in this study have been published by Schafer and Russell (15).

In addition, a sample of finely ground Colorado peat was used to indicate some of the properties that might be shown by organic soil colloids. This sample was autoclaved for 1 hour at 10–15 pounds' pressure to hydrolyze its labile constituents and leave a material that would be stable throughout subsequent experiments.

The two bentonites, illite, and peat were washed with 0.05 N HCl until virtually free of replaceable bases. The Wyoming bentonite was pretreated with NH_4Cl to facilitate solution of gypsum. The four materials were then washed with water or with water-methanol mixtures until chlorides could no longer be detected in the washings. The materials were then air-dried and ground to pass a 60-mesh screen. Since the kaolinite as received was virtually free of replaceable bases, no pretreatment to produce the acid clay was necessary.

The replaceable bases remaining in the acid colloids were determined by washing the clays with NH_4 -acetate, evaporating the washings to dryness, and igniting the residue to destroy the acetate ion. This residue was then dissolved in

an excess of standard HCl, heated to boiling, and the remaining HCl determined by back titration with NaOH to phenolphthalein. The HCl neutralized was considered equivalent to the total replaceable bases, though it is recognized that replaceable Fe and Al could be present in the clays and not be detected as bases by this procedure. Replaceable Ca was then determined in the titrated solution.

Following the NH_4 -acetate washings, the colloids were washed with 0.5 N CaCl_2 until free of NH_4 and then with water or water-methanol mixtures until free of Cl. Finally they were washed with NH_4 -acetate until free of Ca, and the total exchange capacity was determined by measuring the amount of Ca in this

TABLE 1

Percentage Ca saturation, percentage total base saturation, base-exchange capacity, and pH of several types of colloids

TYPE OF COLLOID	PERCENTAGE SATURATION WITH Ca	PERCENTAGE SATURATION WITH ALL BASES	BASE-EXCHANGE CAPACITY	pH*
			m.e.†	
Illite	44	56	28	4.2
Illite	65	78	28	4.9
Illite	85	97	28	6.0
Wyoming bentonite.	42	55	93	4.6
Wyoming bentonite	62	75	93	5.2
Wyoming bentonite	84	96	93	6.3
Peat	39	39	90	4.6
Peat	60	60	90	5.3
Peat	76	76	90	6.2
Kaolinite	40	40	2.7	6.0
Kaolinite	60	60	2.7	6.4
Kaolinite	80	80	2.7	6.8
Mississippi bentonite	42	44	88	4.0
Mississippi bentonite.	62	65	88	4.9
Mississippi bentonite	83	85	86	5.4

* The pH values for illite, the two bentonites, and peat were measured in suspensions containing approximately 1.0 m.e. replaceable Ca per 100 cc. The pH values for kaolinite were measured in suspensions containing approximately 0.5 m.e. replaceable Ca per 100 cc.

† Per 100 gm. dry material.

NH_4 -acetate washing. In this and in subsequent work Ca was determined volumetrically by oxidation of the oxalate with $\text{Ce}(\text{SO}_4)_2$, following precipitation and washing in a centrifuge tube.

Samples of the acid colloids were then suspended in water, and sufficient $\text{Ca}(\text{OH})_2$ was added to bring them to approximately 40, 60, and 80 per cent Ca saturation. After the suspensions had stood, with frequent shaking, for at least 6 weeks, aliquots were withdrawn and analyzed for replaceable Ca, total replaceable bases, and total exchange capacity by the methods described. The results of these analyses, as well as the pH values of the suspensions, are given in table 1. Replaceable Ca as determined would also include any Ca remaining in true

solution in the intermicellar liquid. Since none of the colloids were completely saturated with Ca, however, and considerable time had elapsed since Ca treatment, it is believed that the amount of Ca in this form would be small.

Since the exchange capacity of kaolinite was so low, errors in its determination within the limits of precision of the methods used would cause relatively large errors in determining percentage Ca saturation. For this reason the values for Ca saturation cannot be considered to be so well defined in kaolinite as in the other materials.

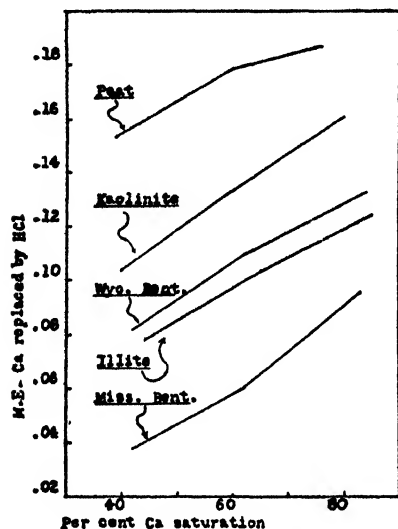


FIG. 1. AMOUNT OF Ca REPLACED BY AN EQUIVALENT AMOUNT OF HCl AS AFFECTED BY PERCENTAGE Ca SATURATION

0.25 m.e. of replaceable Ca + 0.25 m.e. HCl in 250 cc.

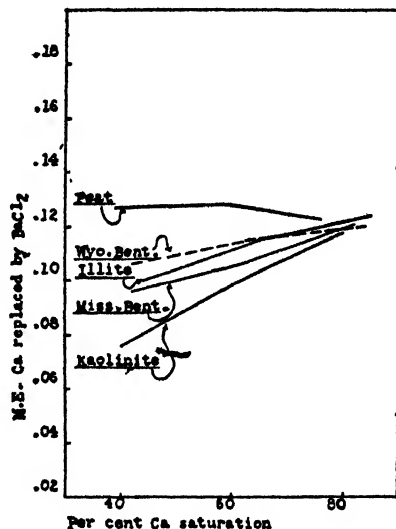


FIG. 2. AMOUNT OF Ca REPLACED BY AN EQUIVALENT AMOUNT OF BaCl_2 AS AFFECTED BY PERCENTAGE Ca SATURATION

0.25 m.e. of replaceable Ca + 0.25 m.e. BaCl_2 in 250 cc.

EXPERIMENTAL

Release of replaceable Ca by equivalent amounts of HCl or BaCl_2

In order to measure the differences in the replaceability of the calcium of these colloids by H ions, an amount of colloidal suspension which would contain 0.25 m.e. of replaceable Ca was mixed with 0.25 m.e. of HCl in a volume of 250 cc. The mixtures were shaken at intervals for 12 hours, and after 24 hours 200 cc. of the supernatant liquid was removed and analyzed for Ca. The total amount of Ca replaced was then calculated, and the results are shown in figure 1. As would be expected from mass action considerations, the amount of Ca replaced increased as the percentage Ca saturation increased. (It should be noted that the HCl added to the system was equivalent to the replaceable Ca and not to the total exchange capacity.) The colloids are arranged in the order peat > kaolinite > Wyoming bentonite and illite > Mississippi bentonite according

to the amount of calcium released. There was a marked difference in the replaceability of the calcium of the two bentonites, the release from Wyoming bentonite being approximately twice as great as that from Mississippi bentonite.

The amount of calcium that could be replaced by an equivalent amount of BaCl_2 was determined by approximately the same technique used for determining the replacement by HCl . The Ba contained in the 200-cc. aliquot of the supernatant liquid was precipitated by a slight excess of H_2SO_4 and removed before precipitation of the calcium. The amounts of calcium replaced are shown in figure 2. Comparison of figures 1 and 2 shows that there was much less difference between colloids in the amount of Ca replaced by Ba ions than in the amount replaced by H ions. Extrapolation of the lines in figure 2 to 100 per cent Ca saturation would give nearly the same value for all colloids.

In peat, the amount of calcium replaced by barium was almost independent of the degree of calcium saturation.

Availability to soybean seedlings of replaceable Ca of various colloids

Availability to plants of the replaceable Ca of these colloids was determined by growing soybeans in mixtures of the colloids with acid-washed sand. The technique used was essentially the same as that described by Albrecht and his associates (1). An amount of colloidal suspension containing 1.0 m.e. of replaceable Ca was mixed with sufficient acid-washed quartz sand to make the total dry weight 750 gm. This mixture was then placed in a $\frac{1}{2}$ -gallon glazed pot, and each pot was planted with five carefully graded Lincoln soybean seeds. At the same time a number of similar seeds were sprouted in cleaned sand and used to replace any seeds failing to germinate in the pots. The few replacements necessary were made before the cotyledons of any of the seedlings had unfolded. The moisture content was maintained between 15 and 20 per cent by frequent additions of distilled water.

In order to eliminate variations in plant growth which might arise from a slow liberation of nutrients other than calcium by weathering of certain of the colloids, each pot received 0.03 millimol of each the following supplemental nutrients: KNO_3 , KH_2PO_4 , MgSO_4 , and MgNO_3 .

These nutrients were added in solution in three equal additions 7, 10, and 14 days after planting. Each pot also received 5 cc. of a 0.2 per cent ferric citrate solution and 5 cc. of Hoagland and Snyder's (11, p. 431) A-Z minor-element solution. Thus, the total amount of cations added as supplemental nutrients was less than one fourth of the replaceable Ca present. Since it has been shown (2) that Ca is the first nutrient which must be supplied to soybean seedlings, it is likely that the plants were not appreciably benefited by these additions, but they were made in order to provide more uniform conditions in all the systems. The amounts added were small in order that release of replaceable calcium by cations from the nutrient additions would be kept at a minimum.

The treatments were replicated three times, and the pots in each replication were placed in a random order, which was changed daily after germination began.

The pots were placed on tables before the south windows of a laboratory. The experiment was conducted during the winter months when the south windows received direct sunlight.

Although the sand-clay cultures made up from kaolinite contained much more clay than those made up from other materials, the ratio of sand to clay was wide in all cases and the physical properties of the cultures, as indicated by root distribution were generally satisfactory. It seems unlikely that any differences in plant growth were due to this factor.



FIG. 3. GROWTH OF SOYBEANS AT HIGH DEGREES OF Ca SATURATION

3 Illite 85 per cent Ca-saturated; 6 Wyoming bentonite 84 per cent Ca-saturated; 9. Peat 76 per cent Ca-saturated, 12. Kaolinite 80 per cent Ca-saturated, 15 Mississippi bentonite 83 per cent Ca-saturated.

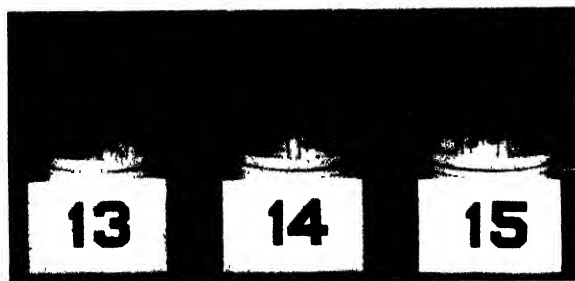


FIG. 4. EFFECT OF PERCENTAGE Ca SATURATION ON GROWTH OF SOYBEANS ON MISSISSIPPI BENTONITE

13. 42 per cent Ca-saturated, 14 62 per cent Ca-saturated; 15 83 per cent Ca-saturated.

The first replication was harvested after a growth period of 21 days and the second and third replications after 25 days. The tops were removed, and the roots were then washed free of sand and colloidal material with distilled water. The tops and roots from each pot were then combined, digested with HNO_3 and HClO_4 until clear, and the silica was filtered off. Ca was then determined in the filtered solution. Use of the semimicroprocedure permitted determination of the calcium content of the plants from each individual pot, even though the amount present was small.

The appearance of some of the plants at harvest time is shown in figures 3 and 4. The amounts of Ca taken up by the plants are shown in figure 5. In general

the plants appeared to be growing normally at harvest time. Symptoms of extreme calcium deficiency were evident only in the plants growing on Mississippi bentonite at the lower degrees of saturation. The size and appearance of the plants did not serve as an infallible indicator of the amount of calcium taken up. This was particularly true of the plants which took up the higher amounts of calcium. The amount of calcium contained in the seed was deducted from that found in the plants to determine the amount taken up from the colloid. The Ca content of five seeds could be predicted with an accuracy of about 3 per cent.

Analysis of the data (16) on Ca absorption indicated that differences greater than 0.036 m.e. Ca between the averages for the three replications would probably be significant at the 5 per cent point.

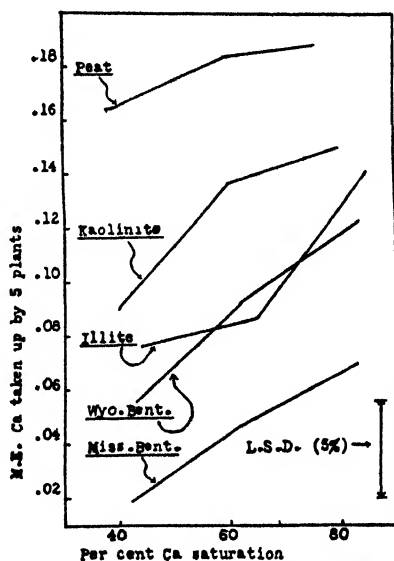


FIG. 5. Ca TAKEN UP BY FIVE SOYBEAN PLANTS FROM 1.0 M.E. REPLACEABLE Ca AS AFFECTED BY TYPE OF COLLOID AND PERCENTAGE Ca SATURATION

The colloids are arranged in the order peat > kaolinite > illite and Wyoming bentonite > Mississippi bentonite according to the availability of their replaceable Ca to the soybeans. In every colloid the availability of replaceable Ca was increased by increases in percentage Ca saturation.

DISCUSSION

The variations in the amount of Ca replaced from the different colloids by an equivalent amount of HCl apparently cannot be attributed entirely to differences in the acidoid strength of the various colloids. For example, examination of the relationship between pH and percentage saturation with all bases (from table 1) would indicate that the two bentonites and illite are similar in their acidoid strength. Wyoming bentonite and illite, however, released about twice as much Ca to the HCl as was released by Mississippi bentonite. It must

be assumed, therefore, that Mississippi bentonite holds Ca more tenaciously than does Wyoming bentonite or illite. Jenny and Ayres (8) have pointed out that the amount of a replaceable ion that will be removed from a colloid by an equivalent amount of another ion is dependent upon the ratio of the oscillation volumes of the two ions. The variation in the amount of Ca replaced by HCl from the different colloids would, therefore, indicate a difference in the ratio of the oscillation volumes of Ca and H ions on these colloids.

Since the amounts of Ca replaced by Ba ions (fig. 2) tend to be similar in all of the colloids at high degrees of Ca saturation, it is evident that the ratios of the oscillation volumes of Ca and Ba are similar for the five colloids studied, and since about one half the Ca was replaced at high degrees of Ca saturation, it seems likely that this ratio is near unity. Differences in the replaceability of Ca at lower degrees of Ca saturation may be attributed to differences in the replaceability of the complementary H ions. The fact that the replaceability of Ca on peat was not greatly affected by the percentage Ca saturation indicates that peat holds H ions so tightly, in comparison with Ca and Ba, that at equilibrium very few H ions were removed from the colloid. This is supported by the observation that the addition of BaCl₂ to a suspension of peat did not change the pH of the suspension as much as did additions of BaCl₂ to suspensions of the other colloids.

The fact that peat and kaolinite released Ca in exchange with HCl more readily than did colloids of the 2:1 lattice type may indicate important differences in the rate of depletion of bases in soils by the leaching action of rains. It would be expected from these results that soils with kaolinitic colloids would become depleted of bases and reach an advanced state of maturity more rapidly than soils with montmorillonitic or illitic colloids.

The results of the experiment on the availability to soybeans of the Ca from the various colloids are in general agreement with those reported by Mehlich and Colwell (10). The order of Ca availability from peat, kaolinite, and montmorillonite was similar to that found in their studies. In their experiments, however, the availability of the replaceable Ca of kaolinite was not affected by increases in Ca saturation above 40 per cent, whereas in the present investigation Ca availability increased with increases in Ca saturation up to 80 per cent. This difference may be due to differences in the amount of Ca offered per plant. Mehlich and Colwell used as much as 100 times the amount of Ca offered per plant in this study.

The pronounced differences in the availability to soybeans of the calcium from the various colloids studied indicate that a knowledge of the nature of the exchange complex is likely to be of value in predicting the Ca fertility of any soil. Under the conditions of this experiment the availability of the calcium was influenced more by the nature of the colloid than by the degree of Ca saturation. For example, replaceable Ca was more readily available when held by peat at 40 per cent Ca saturation than by any of the mineral colloids at 80 per cent saturation. Also, kaolinite at 40 per cent Ca saturation supplied the plants with more calcium than did Mississippi bentonite at 80 per cent saturation.

The difference in replaceability and availability to plants of the Ca from the two bentonites is of interest. Both of these clays are well-authenticated members of the montmorillonite group (4). The base-exchange capacity, however, may be the result of different types of lattice substitution in the two clays. The particle size may also have an effect on the availability of their replaceable Ca. About 12 per cent of the exchange capacity of the Wyoming bentonite was occupied by Mg, and this may have increased the replaceability and availability of Ca from this clay. The difference between these two clays indicates, however, that generalizations concerning the replaceability and availability to plants of Ca from the montmorillonite group of clay minerals are to be avoided unless based upon observations of these properties in a number of examples of

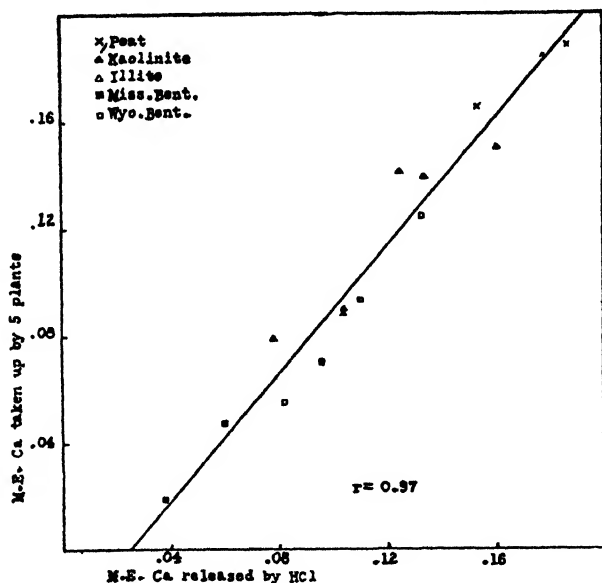


FIG. 6. RELATION OF AMOUNT OF Ca REPLACED BY AN EQUIVALENT AMOUNT OF HCl TO AMOUNT OF Ca TAKEN UP BY FIVE SOYBEAN PLANTS

the group. It is possible that similar variations might be evidenced by the illite group of clay minerals.

The relation between the amount of Ca replaced by an equivalent amount of HCl and that taken up by soybean plants is shown in figure 6. It is evident that an extremely close relationship exists between these two properties of the replaceable Ca. This suggests that in measuring the available soil Ca by laboratory tests, data on the amount of Ca brought into solution by a small amount of an acid replacing agent would be more informative than would a measure of the total replaceable Ca.

The close relationship between the amounts of Ca taken up by plants and the amounts replaced by H ions offers additional support to the theory that plant feeding is essentially a replacement of nutrient cations from the soil by H ions from the plant.

The agreement between availability of Ca to plants and its replaceability by H ions from HCl as found in this study, and also by Mehlich and Colwell, is in sharp contrast to the behavior of K and Zn as reported by Elgabaly, Jenny, and Overstreet (3). The reasons for this pronounced difference between Ca and K or Zn in this respect merit further investigation. Since availability to plants and replaceability by H ions from HCl were so closely related in this study it is unnecessary to consider a "contact effect" in explaining the entrance of Ca into the plant. This does not necessarily prove, however, that Ca did not enter the plant through a process of contact exchange; it indicates only that the Ca was removed from the colloid in an exchange with H ions.

SUMMARY

The availability to soybean seedlings, replaceability by H ions, and replaceability by Ba ions of the replaceable Ca of five colloids were measured. The colloids included kaolinite, illite, two bentonites, and peat, each of which was studied at three degrees of Ca saturation. The results were as follows:

The order of availability to soybeans of the replaceable Ca from the various colloids was peat > kaolinite > illite and Wyoming bentonite > Mississippi bentonite.

In every colloid the availability of the replaceable Ca was increased by increases in percentage Ca saturation.

The two bentonites, both of which are considered to be good examples of the montmorillonite group, showed a considerable difference in the replaceability and the availability to plants of their replaceable Ca.

The amounts of Ca taken up by the soybean plants were very closely related to the amounts replaced by an equivalent amount of HCl.

There was little difference, particularly at high degrees of Ca saturation, in the replaceability by Ba ions of the replaceable Ca of the five colloids studied.

The amounts of Ca taken up by the plants were not related to the amounts replaced by Ba ions.

These results suggest that soils with different types of colloids may show marked differences in the availability of their replaceable Ca, and that the amount of Ca replaced from the soil by a small amount of an acid offers promise as a measure of the Ca fertility of that soil.

REFERENCES

- (1) ALBRECHT, W. A., AND MCCALLA, T. M. 1938 The colloidal clay fraction of soil as a cultural medium. *Amer. Jour. Bot.* 25: 403-407.
- (2) ALBRECHT, W. A. 1940 Adsorbed ions on the colloidal complex and plant nutrition. *Soil Sci. Soc. Amer. Proc.* 5: 8-16.
- (3) ELGABALY, M. M., JENNY, H., AND OVERSTREET, R. 1943 Effect of type of clay mineral on the uptake of zinc and potassium by barley roots. *Soil Sci.* 55: 257-263.
- (4) GRIM, R. E., AND ROWLAND, R. A. 1942 Differential thermal analysis of clays and other hydrous materials: I. *Amer. Mineral.* 27: 746-761.
- (5) HENDRICKS, S. B., AND ALEXANDER, L. T. 1940 Semiquantitative estimation of montmorillonite in clays. *Soil Sci. Soc. Amer. Proc.* 5: 95-99.
- (6) HORNER, G. M. 1936 Relation of the degree of base saturation of a colloidal clay by calcium to the growth, nodulation and composition of soybeans. *Missouri Agr. Exp. Sta. Res. Bul.* 232.

- (7) JARUSOV, S. S. 1937 On the mobility of the exchangeable cations in the soil. *Soil Sci.* 43: 285-303.
- (8) JENNY, H., AND AYRES, A. D. 1939 The influence of the degree of saturation of soil colloids on the nutrient intake by roots. *Soil Sci.* 48: 443-459.
- (9) MARSHALL, C. E., AND KRINBILL, C. 1942 The clays as colloidal electrolytes. *Jour. Phys. Chem.* 46: 1077-1090.
- (10) MEHLICH, A., AND COLWELL, W. E. 1943 Influence of nature of soil colloids and degree of base saturation on growth and nutrient uptake by cotton and soybeans. *Soil Sci. Soc. Amer. Proc.* 8: 179-184.
- (11) MEYER, B. S., AND ANDERSON, D. B. 1939 Plant Physiology. Van Nostrand Co., Inc., New York.
- (12) PIERRE, W. H. 1931 Hydrogen ion concentration, aluminum concentration in the soil solution and percentage base saturation as factors affecting plant growth on acid soils. *Soil Sci.* 31: 183-207.
- (13) PIERRE, W. H., AND ALLAWAY, W. H. 1941 Calcium in the soil: II. Biological relations. *Soil Sci. Soc. Amer. Proc.* 6: 16-26.
- (14) SCHACHTSCHABEL, P. 1940 Untersuchungen über die Sorption der Tonmineralien und organischen Bodenkolloide, and die Bestimmung des Anteils dieser Kolloide in der Sorption im Boden. *Kolloidchem. Beihefte* 51: 199-276.
- (15) SCHAFER, G. B., AND RUSSELL, M. B. 1942 The thermal method as a quantitative measure of clay mineral content. *Soil Sci.* 53: 353-364.
- (16) SNEDECOR, G. W. 1938 Statistical Methods. Collegiate Press, Ames, Iowa.

EFFECT OF MULCHES ON SOIL PROPERTIES

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Western Oregon has a large quantity of grain straw and the residues from various seed crops and other similar materials of potential value for mulching. Only a small portion of these materials is used for bedding in stables or applied directly to the soil. The burning of stubble and of straw stacks is a common practice. A study to define more accurately the value of such waste products, especially when used as a mulch, should be conducive to their conservation and more effective utilization, particularly since orcharding and small-fruit production in western Oregon lend themselves to mulching practices.

These are the considerations that prompted this study to determine the effect of mulching upon the conservation of moisture, the nutrient supply for crop production, and the structure of the soil.

METHODS

In April, 1939, six plots each 15 feet square were laid out with surrounding trenches, 6 feet deep and 2 feet wide, to prevent withdrawal of moisture by roots of plants outside the individual plots. The trenches were maintained by yearly cleaning, and to ensure minimum evaporation from their side walls they were covered with planks, over which soil was placed.

On each of these plots, which were treeless, a different treatment was started immediately, as follows: (a) uncultivated volunteer weeds and average grass sod of the same type as in an adjacent orchard, not mowed; (b) surface scraped sufficiently to remove all growth, beginning in April and repeated as often as necessary to prevent growth from starting; (c) cultivated to a depth of 6 inches to make a fine mulch, with cultivation repeated according to seasonal needs to maintain the mulch; (d) spaded once yearly in April to a depth of 6 inches, but no other pulverization of the soil—any weeds or grass that appeared were pulled by hand; (e) mulched with straw applied in April and renewed yearly to provide a depth of 6 inches when settled; (f) trashy mulch which consisted of volunteer weeds, grass, and vetch pulled at intervals from outside areas and piled on the plot to maintain a settled depth of 6 inches.

Samples of soil were taken for moisture at semimonthly intervals from April through November in 1939, except during September when no help was available. Samples taken under the spread of a 22-year-old apple tree in the adjacent orchard in sod were used for comparison with the plot studies. The

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data for the semimonthly moisture determinations were averaged each month to give the average moisture supply in the soil.

The soil was Willamette loam, fairly mellow and friable near the surface but somewhat sticky in the deeper layers. The wilting points² determined by the sunflower method (12) at 1-foot intervals were 10.4, 11.8, 12.6, 18.9, 21.0, and 20.6 per cent for the 1-, 2-, 3-, 4-, 5-, and 6-foot levels, respectively. The total percentage of moisture in the soil at any particular time is equal to the moisture content above the W.P. as given in the tabulation of results, plus the W.P. value for the soil level involved.

Nitrates were determined by the phenoldisulfonic acid method on soil samples taken 2 years after the plot treatments were started. Organic matter was determined by the method of Walkley and Black (11).

After 3 years of plot treatment, samples were taken for chemical analyses to determine how much calcium and potassium had been leached from the mulching materials into the soil and the depth to which the effect could be detected. The amounts of calcium and potassium soluble in 0.05 *N* HCl were determined.

For this study 10 gm. of soil was treated with 150 ml. of 0.05 *N* HCl, warmed for a few minutes to approximately 60°C., and filtered. Leaching with cold acid was continued by adding small portions at a time, using a small Gooch crucible and suction. A total of 500 ml. of acid was leached through the soil to remove soluble and exchangeable calcium and potassium. Calcium was precipitated as oxalate and titrated as usual with permanganate. Potassium was determined by the cobaltinitrite method of Hibbard (8), asbestos oxidized with permanganate being used for filtering.

Aggregation measurements were made on samples taken in 1942 at depths of 0-1, 1-2, 2-4, and 4-6 inches, and on samples taken in 1943 at depths of 0-3, 3-6, 6-9, and 9-12 inches. The Bouyoucos method (3) was used for mechanical analysis and also the wet-sieve method for the larger aggregates. Only aggregates larger than 1.0 mm. in diameter were determined on the 1943 samples.

The Bouyoucos method (4) was used in a somewhat modified form for aggregate determinations on samples taken in 1942, after the soils were mashed to eliminate large clods, dried, and weighed into cylinders to soak overnight. The cylinders then received 5 ml. of *N* NaOH as a stabilizer, and were up-ended 20 times to get all the soil into suspension. Readings were made at the same time-intervals as in the mechanical analysis, and the data were compared with the results from mechanical analysis to arrive at the degree of aggregation.

For the wet-sieve analysis, 50 gm. of water-free soil, well mixed but not ground, was weighed into a 1-mm. sieve, which in turn was placed in a pan. It was found that sieves should be 5 or more inches in diameter to work well.

Distilled water was added to the pan until the level in the sieve was above the level of the soil and the sieve was about three fourths full of water. The soil was allowed to soak 1 hour. Then the sieve, with soil immersed, was rotated ten times in 5 seconds so as to roll the particles about gently. After the ten rotations, the sieve was lifted from the water. Immersion, rotation, and lifting

² W. P. will be used to designate the wilting point in this paper.

of the sieve from the water were repeated until the procedure had been carried out ten times. This constituted the first washing, which removed most of the loose soil and left on the sieve those granules larger than 1 mm. At the end of the first washing, the water and the loose soil in the pan were discarded.

The soil remaining on the sieve was given a second washing similar to the first, the water again discarded, and the pan cleaned.

The sieve was replaced and left standing overnight in clean distilled water before the third washing, which followed the same procedure as the previous washings and was designed to remove any remaining loose particles of soil. Again the water was discarded and a fourth washing made with ten immersions but with an up-and-down movement instead of the rotary motion. The water remained clear after this washing, and granules of soil were left on the sieve.

After the washings, the soil in the sieve was dried and weighed. This weight multiplied by 2 was the percentage of the sample having aggregates larger than 1 mm. in diameter. This arbitrary procedure was standardized so that all soils

TABLE 1
Rainfall and evaporation records from April to November at site of experiment

	APRIL	MAY	JUNE	JULY	AUGUST	OCTOBER	NOVEMBER
Rainfall 1939..... inches	0.22	1.71	0.70	0.43	1.14	2.90	0.31
Evaporation 1939..... inches	3.4	4.5	4.6	7.5	6.3
Relative humidity 1939*.. per cent	53.8	54.2	57.3	47.5	46.1	71.2	82.0
Normal rainfall							
Quantity..... inches	2.43	1.69	1.15	0.33	0.45	2.90	6.92
Proportion of annual rainfall (40.25 inches).. per cent	6.04	4.19	2.86	0.82	1.12	7.20	17.19

* Mean relative humidity for the year 1939 was 65.6 per cent.

were treated alike. Repeated determinations placed the soils in the same order of magnitude as to degree of granulation.

RESULTS OF STUDY

Effect of mulches on soil moisture

A study of the moisture data indicates that the grass and volunteer weed growth had their principal effect in August after a prolonged period of scant rainfall (tables 1 and 2). The effect was greatest in the top foot (table 2) but was considerable in the second foot (table 3). The rough-spaded and the scraped plots dried to about the W.P. in August in the first foot. Only the uncultivated sod and the sod orchard approached the W.P. in the second-foot depth. The moisture remained highest under the straw mulch in both the surface and the second foot in the dry part of the season. Trash mulch was somewhat superior to tillage in the surface foot. The low figure for July would appear to be an error of sampling, since the August figure was much higher. Though the trash mulch was next best to the straw mulch for saving moisture through July and

August in the second-foot depth, the difference compared to spaded rough or tillage mulch was of doubtful significance. Sod, as would be expected, depleted moisture both in the orchard and on the plots. This depletion extended into the second foot, and was most pronounced during July and August, after a period of low rainfall, low humidity, and high evaporation. The low figure for the moisture in the second-foot depth of the sod orchard in October may have been due in part to the protecting cover of foliage which prevented much of the October

TABLE 2

Average moisture content above the W.P. for the surface foot of soil from April to November, 1939

TREATMENT	MOISTURE CONTENT ABOVE W.P.						
	April	May	June	July	August	October	November
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
a. Uncultivated sod.....	10.7	6.7	5.1	1.7	-1.7	8.3	13.0
b. Scraped.....	7.9	8.6	7.5	3.8	0.0	6.2	12.0
c. Tillage mulch.....	10.2	12.5	13.2	8.4	3.6	11.1	14.7
d. Spaded rough.....	6.1	9.8	8.9	7.1	-0.8	15.4	14.7
e. Straw mulch.....	17.9	16.3	18.6	17.9	16.3	18.9	19.5
f. Trash mulch.....	16.6	16.1	15.0	3.2	8.8	17.6	18.0
Sod orchard.....	12.7	9.4	6.7	3.2	-0.9	6.6	8.2

TABLE 3

Average moisture content above the W.P., for the second foot of soil from April to November, 1939

TREATMENT	MOISTURE CONTENT ABOVE W.P.						
	April	May	June	July	August	October	November
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
a. Uncultivated sod.....	11.0	6.6	5.1	3.0	2.0	4.9	5.4
b. Scraped.....	10.8	10.1	9.4	8.6	7.3	6.5	6.7
c. Tillage mulch.....	12.3	12.6	11.8	9.3	7.7	8.9	11.0
d. Spaded rough.....	13.3	12.0	12.3	9.6	8.3	9.5	11.0
e. Straw mulch.....	20.5	12.8	14.3	14.5	11.9	12.8	14.1
f. Trash mulch.....	20.0	12.7	11.6	10.3	9.1	9.2	15.5
Sod orchard.....	12.1	9.9	7.0	5.3	4.6	1.7	5.5

rain from reaching the soil. Only the surface foot under the trees had the moisture content built up by the October rains.

Normal rainfall, though somewhat different from the 1939 record, is low during the critical growing months when evaporation and moisture usage are high². This gives added value to a summer mulch for saving water. The percentage distribution of the normal annual rainfall for the seven months reported is shown in the last row of table 1. The best four growing months, May through August, in 1939 had less than 4 inches of rain and nearly 23 inches of evaporation. The

² The evaporation and rainfall data were provided by E. F. Torgerson.

mean relative humidity for the 4 months was only 51.3 per cent, which explains the high evaporation. Normal rainfall is 1.71 inches for September, which is the month of beginning moisture renewal. The normal mean relative humidity for September is 54.6 per cent, compared with 51.3 per cent in 1939. Rainfall was 0.43 inch in September, 1939, and evaporation from a free water surface was 4.7 inches. Not until October or November does the soil become well supplied with water. The mean humidity of the atmosphere rose to 71.2 per cent in October and 82.0 per cent in November, 1939. The moisture content of the soil under straw mulch remained nearly uniform throughout the season of May through October, indicating little loss of moisture in the surface 2 feet even in the driest weather. No other plot showed this constancy of moisture content.

The data of table 4 indicate that the moisture in the third foot of soil remained well above the W.P. throughout the season under all treatments. Only the trees removed material amounts of moisture at this depth, and principally in the latter part of the season. If the whole season is averaged, the tillage mulch maintained

TABLE 4
Moisture above the W.P. in the third foot of soil from April to November, 1939

TREATMENT	MOISTURE CONTENT ABOVE W.P.						
	April	May	June	July	August	October	November
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
a. Uncultivated sod	16.9	16.2	15.7	10.0	13.9	15.4	15.0
b. Scraped	16.3	13.8	15.0	12.5	12.7	12.4	12.7
c. Tillage mulch	17.3	18.5	17.7	15.0	16.5	15.8	19.7
d. Spaded rough	18.4	16.4	17.1	13.7	11.8	14.4	16.6
e. Straw mulch	15.7	11.6	12.8	11.9	13.0	12.0	14.1
f. Trash mulch	18.7	13.6	13.7	12.4	13.1	12.6	12.5
Average	17.2	15.0	15.3	12.6	13.5	13.8	15.1
Sod orchard	15.2	14.8	12.6	11.8	9.8	10.6	10.4

a somewhat higher moisture content than the other treatments in the third foot of soil. This is evidence that tillage does not bring moisture from the deep soil to the surface, as some growers maintain. The deep soil is heavier in texture than the surface, and natural processes do not permit appreciable movement of moisture from the small capillaries of a heavy soil to the large capillaries of the more open soil above. By the laws of physics, moisture moves from a larger capillary to a smaller but not *vice versa*. The data indicate also that the October and November rains had not yet restored the soil moisture removed from the third foot in the orchard. Tillage mulch and spaded rough treatments show the greatest water infiltration with the fall rains.

The data of table 5 show the superior moisture-saving capacity, in terms of precipitation inches, of straw mulch over other treatments. Thus, the tillage mulch plot during July and August had 2.4 inches less water above the W.P. than did the straw mulch plot. The rather heavy rainfall of October eliminated much of this difference by restoring the moisture of the tillage-mulched soil.

A large portion of this rain was absorbed in the straw and trash mulches, and therefore wetting of the soil under the mulch was restricted as compared with the cultivated plot. The saving of moisture effected by the straw mulch was often greater than the rainfall during the summer season and was equivalent to 3 or 4 inches of rain in some cases. The trash mulch, spaded rough, and tillage mulch treatments were nearly as good as straw mulch. The sod orchard showed great-

TABLE 5

Water deficiency for several plot treatments for each month as compared to moisture present under straw mulch, for the surface 3 feet of soil, 1939

Results in equivalent inches

TREATMENT	WATER DEFICIENCY						
	April	May	June	July	Aug.	Oct.	Nov.
	<i>in.</i>	<i>in.</i>	<i>in.</i>	<i>in.</i>	<i>in.</i>	<i>in.</i>	<i>in.</i>
a. Uncultivated sod.	2.8	2.0	3.5	5.2	3.9	2.7	4.0
b. Scraped.	3.4	1.5	2.4	3.4	3.6	3.3	2.9
c. Tillage mulch.	2.6	0.0	0.5	2.4	2.4	1.4	0.4
d. Spaded rough.	2.9	0.5	1.3	2.5	3.7	0.8	1.0
f. Trash mulch.	0.0	0.5	1.0	3.3	1.8	0.7	0.3
Sod orchard.	2.5	1.2	3.4	4.2	4.7	4.4	3.6
Rainfall.	0.22	1.71	0.70	0.43	1.14	2.90	0.31

TABLE 6

Moisture above the W.P. in the lower 3 feet of a 6-foot profile for 1939

TREATMENT	MOISTURE CONTENT ABOVE W.P.				
	June	July	August	October	November
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
a. Uncultivated sod.	17.0	15.2	15.2	15.3	15.1
b. Scraped.	17.0	16.0	15.5	15.0	16.5
c. Tillage mulch.	18.0	15.7	14.8	14.9	15.0
d. Spaded rough.	17.0	16.3	14.2	15.3	15.2
e. Straw mulch.	16.8	16.1	16.3	15.2	15.1
f. Trash mulch.	17.2	16.2	15.5	14.0	16.8
Sod orchard.	15.4	14.7	11.5	9.6	10.1
Average of 6 plots (sod orchard omitted).	17.1	15.9	15.3	15.0	15.6
Removal by trees (difference between uncultivated sod and sod orchard).....	1.6	0.5	3.7	5.7	5.0

est exhaustion of soil moisture in late summer, probably because of the deeper roots of the trees.

The average W.P. of the lower 3 feet of a 6-foot profile of this soil is 20.2 per cent. The data of table 6 indicate that the mulches have had little effect in saving moisture at this depth because little moisture was lost from any but the orchard plot. The deep roots of the trees partially exhausted the moisture of the orchard soil. Not more than half of the usable water was removed in the orchard

by the combined effect of the grass and the trees. Very little moisture had been removed from any of the other plots, even at the end of the season, because the roots of grasses apparently did not penetrate to this depth. This is indicated by the data on the sod plot, which are nearly the same as the averages for all the treeless plots. These averages are so nearly the same for the months after June that it is safe to conclude that little moisture was lost at this depth by evaporation, drainage, or plant removal. If the removal of moisture by the trees may be assumed to be the difference between the moisture in the uncultivated sod plot and that under the trees, the data show a tendency toward progressive removal to October. The October and November rains did not wet the soil appreciably at this depth.

TABLE 7

Moisture above the W.P. and nitrates in the top foot of soil under various treatments, 1941*

TREATMENT	DATE SAMPLED				
	May 20	June 18	July 10	Aug. 26	Sept. 29
<i>Moisture content above W.P. (per cent)</i>					
a. Uncultivated sod.	14.5	6.2	1.9	0.0	12.6
b. Scraped	8.7	6.8	6.3	5.2	9.4
c. Tillage mulch.	13.7	11.9	9.3	9.5	11.3
d. Spaded rough.	12.5	11.6	7.0	8.1	10.7
e. Straw mulch.	15.8	11.3	12.3	14.5	17.6
<i>Nitrate content expressed as nitrogen (p.p.m.)</i>					
a. Uncultivated sod.	Tr.	Tr.	Tr.	Tr.	Tr.
b. Scraped	5.6	3.3	6.3	7.8	10.2
c. Tillage mulch	3.3	4.5	15.3	14.0	10.7
d. Spaded rough.	3.8	5.3	11.8	11.4	7.1
e. Straw mulch	4.5	4.0	15.1	12.1	29.6

* Nitrate determinations on the trash mulch plot were lost. Rainfall recordings (in inches) were as follows: May, 2.42; June, 1.03; July, 0; August, 1.09; September, 3.96.

Effect of mulches on nitrates in soil

The data in table 7 show the effect of mulches or other soil conditions on the moisture and nitrate contents in the surface foot of soil. The lack of nitrates in the uncultivated plot is probably due to one of two causes: their removal by vegetative growth, or lack of sufficient moisture (July and August) for their production. The scraped plot had enough available moisture for some nitrate production, even in dry weather. The tillage mulch and the straw mulch were nearly equally good for moisture conservation and for nitrate production. The highest nitrate content was found under straw mulch in September after fall rains had started. The spaded rough plot was intermediate between the mulched plots for both moisture conservation and nitrate production except in the early part of the season. During May and June nitrates were low in all plots. There was little difference at first among the plots in either moisture or nitrate, except that the uncultivated plot never showed more than a trace of nitrate. Moisture

differences began to appear in June, but there was little difference in nitrate until July.

Ballou and Lewis (1) report that on poor soil a straw mulch is valuable for saving moisture and that on soils well supplied with organic matter the straw mulch is valuable for conserving moisture and for aiding the liberation of nitrates. This probably results largely from the action of bacteria using the organic matter present in the soil as a source of energy in the fixing of nitrogen from the air rather than from an actual release of the fixed nitrogen contained in the organic matter.

TABLE 8
*Effect of organic mulches on calcium and potassium content of soil, 1942**

Depth of sample. inches	CALCIUM				POTASSIUM			
	0-1	1-2	2-4	4-6	0-1	1-2	2-4	4-6
	m.e.†	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
<i>Treatment</i>								
Scraped.....	13.4	13.3	13.8	14.3	0.66	0.61	0.52	0.61
Straw mulch.....	15.6	14.2	12.7	12.6	2.67	2.09	1.73	1.11
Trash mulch.....	16.0	15.0	15.2	14.5	1.98	1.68	1.28	0.90

* Soil leached with 0.05 N Hcl.

† Calcium and potassium reported as milliequivalents per 100 gm. of soil.

TABLE 9
Effect of organic mulches on organic matter content of soil after 3 years

Depth of sample. inches	ORGANIC MATTER CONTENT			
	0-1	1-2	2-4	4-6
	per cent	per cent	per cent	per cent
<i>Treatment</i>				
Scraped.....	3.06	2.92	2.86	2.86
Trash mulch.....	4.83	4.04	4.56	4.01
Straw mulch.....	6.73	4.28	3.72	3.26

Effect of mulches on calcium and potassium in soil

The data in table 8 indicate that the organic mulches have had minor effects, if any, on the soluble calcium. Soluble potassium has been greatly increased by the mulches, especially by the straw mulch. The effect is greatest in the surface soil immediately under the mulch, but is noticeable at a depth of 4 to 6 inches. The potassium of plant materials is relatively readily soluble and leaches into the soil. The increase is marked for the 3 years of leaching and accumulation. Gourley (6) reports a marked increase in soluble nitrogen, phosphorus, calcium, potassium, magnesium, and boron under a mulch.

Effect of mulches on soil organic matter

The table in table 9 indicate that the organic mulches had a favorable effect in increasing the organic matter content of the soil. The greatest effect was

caused by the straw in the immediate soil surface. This method of renewing soil organic matter is worthy of consideration where straw is abundant and where the organic matter has been depleted by prolonged cultivation. The more uniform distribution of the organic matter contributed by the trashy mulch may have been due to the activity of earthworms, of the large night-crawler type, introduced into this plot 2 years after the experiment was started.

Effect of mulches on soil aggregation

In calculating the percentage of granulation, each plot was subjected to both mechanical and aggregate analyses. Mechanical analysis showed only small

TABLE 10
*Effect of mulches on soil aggregation after 3 years**

DEPTH OF SAMPLE AND TREATMENT	CLAY AGGREGATED	FINE SILT AND CLAY AGGREGATED	TOTAL SILT AND CLAY AGGREGATED	SAND-SIZE PARTICLES INCLUDING AGGREGATES
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
<i>0-1 inches</i>				
Scraped.....	83.1	73.4	53.3	60.2
Trash mulch.....	90.2	79.6	66.7	73.2
Straw mulch	90.3	90.2	86.1	88.2
<i>1-2 inches</i>				
Scraped.....	85.1	77.1	52.6	59.2
Trash mulch.....	85.9	80.0	63.3	70.2
Straw mulch.....	88.3	82.1	67.4	72.2
<i>2-4 inches</i>				
Scraped....	83.4	77.1	50.9	58.2
Trash mulch.....	85.9	80.0	63.3	72.2
Straw mulch	88.3	82.1	67.4	72.2
<i>4-6 inches</i>				
Scraped.....	85.1	82.1	53.2	60.2
Trash mulch.....	88.3	81.7	67.4	72.2
Straw mulch.....	83.4	80.4	65.0	70.2

* The aggregation figures represent the percentages of each soil fraction, as determined by mechanical analysis, that is aggregated into particles larger than that fraction. Thus the first figure in the first column indicates that 83.1 per cent of the clay was aggregated into particles larger than clay.

variations from one plot to another. The approximate mechanical composition was 15 per cent sand, 44 per cent silt, and 41 per cent clay. Fine silt and clay (15-minute reading) was about 58 per cent. Determinations were in duplicate.

Organic mulches have a favorable effect upon the physical properties of the soil. The data in table 10 show that granulation is promoted by organic mulches. In every case most of the clay is aggregated into some size larger than clay, the clay perhaps serving in part as cement to hold the aggregates together. There is a marked difference in the total silt and clay that is aggregated into particles of sand size or larger. Here the organic materials have had an effect not found in the scraped plot, which was undisturbed except to have the surface growth re-

moved. The effect of the organic materials, though greatest in the top inch, appears to extend down into the fifth and sixth inches, the lowest depth of sampling.

The data in table 11 indicate that the organic mulches increased the proportion of aggregates larger than 1.0 mm. in the surface inch or two of soil, but had less effect at greater depth. The samples taken in 1943 were spaced to extend below the depth of cultivation. There is no apparent reason for the greater aggregation caused by mulches below the tillage depth. The tillage mulch showed somewhat less aggregation than the scraped plot except at depths of 9 to 12 inches. The results of the previous year indicating that organic mulches improve the aggregation of the surface soil were verified. Havis (7) found that organic mulches had a favorable effect in producing aggregates of the larger sizes.

TABLE 11

Effect of organic mulches in producing aggregates larger than 1 mm. in diameter after 3 and 4 years*

Depth of sample inches	AGGREGATES >1 MM. IN 1942 SAMPLE			
	0-1	1-2	2-4	4-6
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
<i>Treatment</i>				
Scraped.....	1.0	1.1	0.8	1.8
Trash mulch.....	23.0	10.3	13.9	5.8
Straw mulch.....	41.6	12.0	5.5	4.1
Depth of sample. inches	AGGREGATES >1 MM. IN 1943 SAMPLE			
	0-3	3-6	6-9	9-12
<i>Treatment</i>				
Scraped.....	4.2	7.7	7.1	2.3
Trash mulch.....	38.0	12.8	9.6	19.6
Straw mulch.....	37.1	11.5	5.6	12.3
Tillage mulch.....	3.8	3.4	4.6	7.4

* Percentage of total sample.

DISCUSSION

The results of this study indicate that organic mulches improve both physical and chemical properties of the soil and that grain straw is a good mulching material. The amount of moisture saved by an organic mulch may be equivalent to one or two additional good rains during the most active growing season. The saving, however, would probably be dependent upon the amount of mulch used. Where there is abundance of straw, mulching might be substituted for tillage for weed control and moisture conservation.

It is apparent that tillage does not improve soil granulation but may have the opposite effect of dispersing the soil. The decomposing mulch on the soil materially increases granulation, especially in the immediate soil surface. This effect

may be due in part to the presence of rotting organic matter and in part to substances produced by soil organisms (9).

The surface protection and improvement in structure should increase the capacity of the soil to absorb water as well as reduce evaporation. At the same time erosion should be reduced, as has often been demonstrated (2). The improved structure of the soil under the mulch was noticeable in the way the soil handled in the taking of samples. Mulching therefore improves soil tilth without cultivation. In fact, prolonged tillage of the soil may have the effect of producing a dispersed or compact structure and poor tilth.

Likewise, the improvement of the nutrient supply in the mulched soils over a period of years should be of considerable importance. Straw mulch after 3 years about doubled the organic matter in the top inch of soil without reducing the capacity of the soil to produce nitrates for plant growth. Soluble potassium was increased severalfold by the straw and somewhat less by the trashy mulch. Seldom, if ever, should a potassium shortage be found where organic mulching is practiced. The danger of a nitrogen shortage should likewise be reduced, especially after the mulch has begun to decompose, since the mulch renews the humus which carries the nitrogen liberated from the organic matter by the process of nitrification. The mulch system has proved satisfactory in orchard production (1, 5, 10).

SUMMARY

Moisture conservation, nutrient supply, and soil structure were compared on six treeless plots under different treatments—uncultivated sod, scraped and kept bare of growth, tillage mulch, spaded rough, straw mulch, and trash mulch—and on an adjacent orchard in sod.

The straw mulch saved moisture equivalent to 2 or 3 inches of rainfall in dry weather. The moisture saving was principally in the upper 2 feet of soil. The trash mulch had a lesser moisture-saving effect.

Nitrates were as high under straw mulch after it had been established for 3 years as under clean cultivation. The soil that was cultivated or mulched with straw was generally higher in nitrates than the plot that was scraped to control vegetation, probably because the scraped plot became drier than the other plots.

The straw mulch caused a marked increase in soluble potassium but little increase in calcium in the topsoil. Trash mulch increased the soluble potassium to a lesser extent than did the straw.

Straw and trash mulches increased the organic matter content of the topsoil.

Both straw and trash caused an increase in the water-stable aggregates. The increase in the larger aggregates was most noticeable.

REFERENCES

- (1) BALLOU, F. H., AND LEWIS, I. P. 1920 Orchard rejuvenation in southern Ohio. Ohio Agr. Exp. Sta. Bul. 339.
- (2) BORST, H. L., AND WOODBURN, R. 1942 The effect of mulching and methods of cultivation on run-off erosion from Muskingum silt loam. *Agr. Engin.* 23: 19-22.

- (3) BOUYOUCOS, G. J. 1928 The hydrometer method for making a very detailed mechanical analysis of soils. *Soil Sci.* 26: 233-238.
- (4) BOUYOUCOS, G. J. 1929 The ultimate natural structure of soils. *Soil Sci.* 28: 27-37.
- (5) CULLIMAN, F. P., AND BAKER, C. E. 1927 Orchard soil management studies. Ind. Agr. Exp. Sta. Bul. 315.
- (6) GOURLEY, J. H. 1943 The fertilizer value of an orchard mulch. *Amer. Fruit Grower* 63: 13.
- (7) HAVIS, L. 1943 Aggregation of an orchard and vegetable soil under different cultural treatments. Ohio Agr. Exp. Sta. Bul. 640.
- (8) HIBBARD, P. L., AND STOUT, P. R. 1933 Estimation of potassium by titration of cobaltinitrite with potassium permanganate. *Jour. Assoc. Off. Agr. Chem.* 16: 137-140.
- (9) MARTIN, J. P., AND WAKSMAN, S. A. Influence of microorganisms on soil aggregation and erosion. *Soil Sci.* 50: 29-47.
- (10) SHAW, J. K., AND SOUTHWICK, L. 1936 Heavy mulching in bearing apple orchards. Mass. Agr. Exp. Sta. Bul. 328.
- (11) WALKLEY, A., AND BLACK, I. A. 1934 An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Sci.* 37: 29-38.
- (12) WORK, R. A., AND LEWIS, M. R. 1934 Moisture equivalent, field capacity, and permanent wilting percentage and their ratios in heavy soils. *Agr. Engin.* 15: 355-362.

ISOHYDRIC pH, pH OF SOIL PASTE, AND pH OF EXCHANGE NEUTRALITY

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Factors contributing to the alkalinity of semiarid soils are of vital importance to the chemical and physical properties and to the productivity of such soils. Hilgard attributed alkalinity largely to sodium carbonate, and he and his contemporaries used quantitative methods to determine alkalinity in water extracts of the soil, expressing the results as percentages of Na_2CO_3 . During the period covered by Hilgard's investigations it was the generally accepted belief that Na_2CO_3 was formed in soils by reactions between NaCl or Na_2SO_4 and CaCO_3 , which are present in virtually all semiarid soils. The later investigations of Gedroiz, Kelley, and others showing that these salts may also react with the clay minerals in the soil and that the resulting products may become actively alkaline by hydrolysis indicated another source of alkalinity and greatly expanded our knowledge of such soils. To these sources of soil alkalinity, the contributions of the Arizona Experiment Station on the direct alkalinity of CaCO_3 should be added, for CaCO_3 has a pH of 9.6 and is present in virtually all semiarid alkaline and saline soils.

Accompanying the development of our knowledge of contributing factors in soil alkalinity have been equally important developments in the electrometric methods of measuring the OH-ion concentration of alkali soils. In the earlier methods the soil was shaken with distilled water, and the pH determination was made on a soil suspension. The soil:water ratios at which these determinations were made are greater than any soil:water ratios ever met under field conditions, and when a soil is shaken with an excess of distilled water, it hydrolyzes and a part of the adsorbed bases go into solution as hydroxides. It is obvious, then, that values thus obtained do not exist naturally. Even if such high soil:water ratios were attained under field conditions, the pH value would not be so high as the values obtained with soil suspensions in distilled water, for irrigation waters and the soil solution are buffered to such an extent as to repress hydrolysis. The development of the glass electrode offered a means for determining the pH of soils at low moisture contents, and on the basis of investigations conducted by the author (4) it was proposed that pH determinations be made on a soil paste at a moisture content approximating the moisture equivalent.

The pH value of a soil is one of many dynamic properties which characterize the soil mass. It responds markedly, therefore, to changes in environment. The ideal method for determining pH should be one in which no hydrolysis takes place or at least no more than will take place under field conditions. Such a value should be close to an absolute pH. Puri and Sarup (7) have proposed the isohydric pH as an absolute value, and Mattson (6) has suggested the pH value representing the point of exchange neutrality. The former is defined as the pH

value of a buffer solution which shows no change in reaction when coming in contact with the soil. The pH of exchange neutrality is that point at which the addition of a neutral salt to a soil suspension does not affect the pH of the latter. In view of the fundamentally sound basis for the use of the "paste" method, it appeared to be of interest to conduct comparative experiments on the pH of the soil paste,¹ the isohydric pH, and the pH of exchange neutrality.

ISOHYDRIC pH

When two solutions, or a solution and a miscible material, have the same hydron concentration they are said to be isohydric. This is probably the basis for the suggestion of Puri and Sarup that the isohydric pH of the soil represents an absolute value. In alkali soils the OH ions are largely confined to the moisture film in immediate contact with the surface of the soil particles, the degree of freedom of circulation depending upon the amount of water present. In a soil paste at a moisture content approximating the moisture equivalent, hydrolysis as well as freedom of circulation is reduced to a minimum. Furthermore, when the soil paste is prepared for the pH determination, a large percentage of the water becomes bound and inactive. Thus in a soil paste the same objective is attained as with buffer solutions in the isohydric method, namely, a minimum degree of hydrolysis.

The buffer solution used for comparison of isohydric values with the pH of the soil paste is the same as that used by Puri and Sarup. It consists of 25 ml. of 0.2 *N* KCl and 25 ml. of 0.2 *N* H₂BO₃, plus varying amounts of 0.2 *N* KOH added before dilution of the whole to 100 ml. to form the complete buffer solution. A series of buffer solutions were prepared to cover the pH range in which the soils would fall, and the pH of each was determined with the glass electrode. Twenty grams of soil was then added to each buffer solution, and the whole shaken for 2 hours. The suspensions were then filtered, pH determinations made on the filtrates with the glass electrode, and the values compared with the pH values of the same buffer solutions before being shaken with soil. In some cases pH determinations were made on the soil suspensions in the buffer solutions to check these values against the filtrates, and perfect agreement between the two was found. The pH values of the soil paste and the isohydric pH values for 22 soils are given in table 1. The saline soils and the black alkali soils are separated for convenience.

The isohydric pH was obtained by plotting the titration data on cross-section paper. One curve was drawn using the abscissa for the pH value of the buffer solution and the ordinate for the pH value of the buffer solution plus soil. The other curve was drawn using the ordinate for the pH of the buffer solution and the abscissa for the pH of the buffer solution plus soil. The point of intersection of the two curves represents the isohydric pH, as illustrated in figures 1 and 2.

The very close agreement between the pH of the soil paste and the isohydric pH in all the saline soils is positive evidence that both methods yield the same pH values; in fact, the agreement between the two methods is as close as duplicate

¹ All soil pastes were prepared with distilled water.

TABLE 1
pH values of soil paste and isohydric pH

SALINE SOILS		BLACK ALKALI SOILS	
Paste*	Isohydric	Paste*	Isohydric
7.90	7.80	8.20	8.15
7.60	7.60	8.95	8.85
7.85	7.80	9.55	9.45
7.75	7.70	10.15	10.10
7.55	7.55	8.30	8.30
7.90	7.90	8.40	8.05
7.75	7.60	9.30	8.85
7.20	7.20	8.50	8.30
8.15	8.10	9.25	9.40
8.15	8.10		
7.60	7.65		
8.40	8.30		
8.15	8.10		

* Prepared with distilled water.

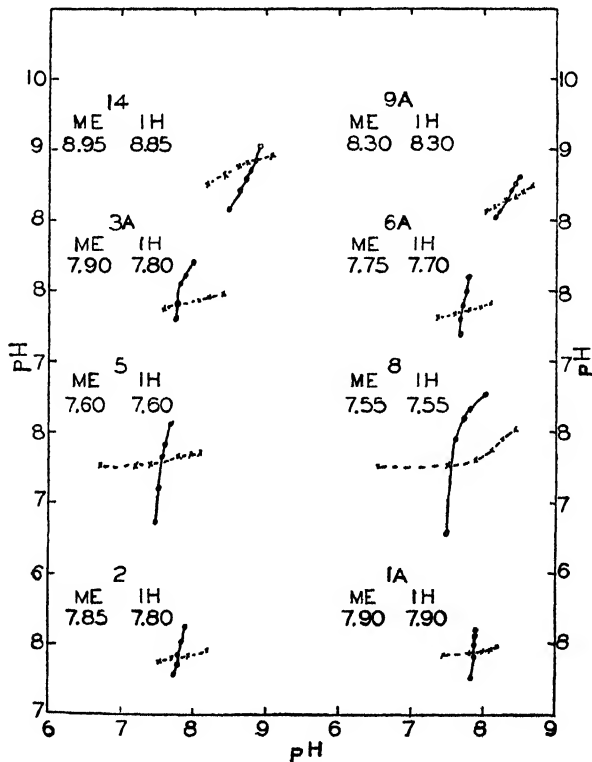


FIG. 1. ISOHYDRIC TITRATION CURVES FOR SALINE SOILS

The pH of soil paste (ME) and the isohydric pH (IH) are given with the titration curves for each soil.

determinations by either method singly. For the black alkali soils, already more or less buffered by $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$, agreement between the two values is close except in two cases. The curves parallel each other so closely, however, in the vicinity of the point represented by the pH of the soil paste that even in these two cases the agreement may be considered satisfactory.

The nature of the curves obtained for the two types of soil, the saline and the alkaline, are significantly different, as shown in figures 1 and 2. For the saline soils (fig. 1) the lines intersect at approximately right angles. The curves for the soils which contain black alkali (fig. 2) tend to parallel each other both above and below the point of intersection. This clearly shows the $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$

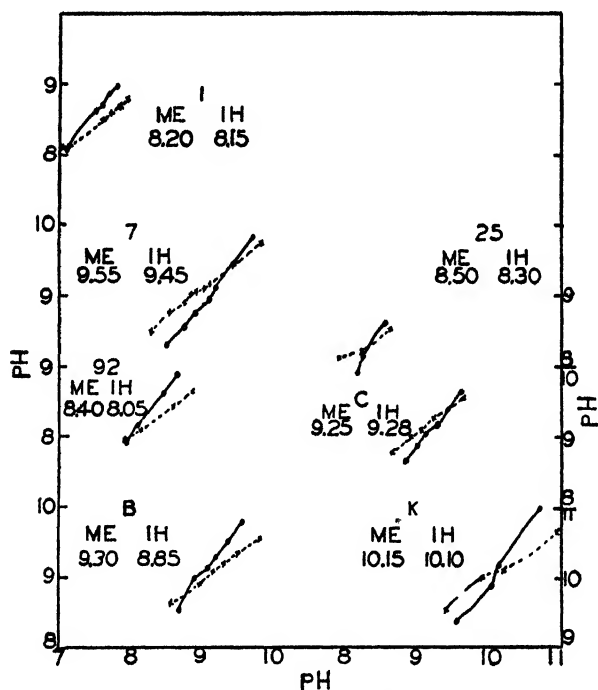


FIG. 2. ISOHYDRIC TITRATION CURVES FOR BLACK ALKALI SOIL

The pH of soil paste (ME) and the isohydric pH (IH) are given with the titration curves for each soil.

buffer effect of the soil itself. Puri and Sarup do not recommend the use of buffer solutions for determining the isohydric pH of black alkali soils. They suggest that the pH of such soils may be calculated from the $\text{CO}_3\text{:HCO}_3$ ratio in the soil and the pH of the soil suspension in a 0.1 N KCl solution.

pH OF EXCHANGE NEUTRALITY

Mattson and Wiklander (6) have emphasized two pH values for soils: the pH of exchange neutrality and the equiionic pH value. The latter represents the pH at which the capacities of the soil to combine with the anions and cations of a solution are equal.

In order to compare the pH of the soil paste, at approximately the moisture equivalent, with the pH of exchange neutrality, three soils were selected. Non-calcareous soils were used in order to avoid the influence of CaCO_3 on the titration of the soil and the "breakdown" in the exchange complex that might accompany the removal of CaCO_3 by treatment of the soil with dilute acid. A suspension of 10 gm. soil in 20 ml. of distilled water and another of 10 gm. soil in 20 ml. of $N \text{ Na}_2\text{SO}_4$ solution were titrated with $0.02 N \text{ H}_2\text{SO}_4$ or NaOH . These titrations were plotted, and the point of intersection of the two curves was taken at the pH of exchange neutrality. The data for these three soils together with the pH of the soil paste are given in figure 3. In every case the pH of the soil paste and the pH of exchange neutrality agree very closely.

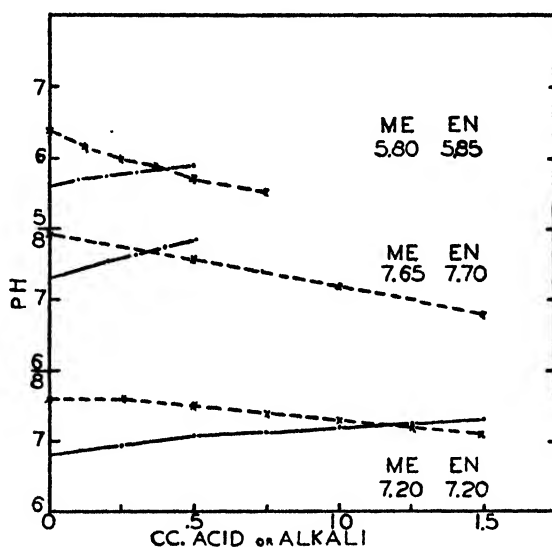


FIG. 3. EXCHANGE NEUTRALITY TITRATION CURVES

The pH of soil paste (ME) and pH of exchange neutrality (EN) are given with each set of curves.

pH AT LOW MOISTURE

Some interest has been manifested in the determination of pH values of soils at moisture contents below the moisture equivalent, even to the point of air-dryness. In the original work on this problem (4) it was shown that equilibrium values could be obtained at moisture contents well below the moisture equivalent. The moisture content represented by the moisture equivalent was selected, however, because the values thus obtained were constant and reproducible. Furthermore, the moisture present in the small pores and that imbibed by the soil colloids are represented by the moisture equivalent, and all soils are equally wet at this point.

Previous to the work in this laboratory Heintze (3) had obtained, with the glass electrode, pH values of 5.6 to 6.2 for dry soils and had concluded that these

values did not represent soil pH values but "the pH value of a thin moist film in equilibrium with the CO₂ content of the air and with the glass but not in equilibrium with soil moisture." More recently Davis (2) attributed these low pH values in dry soils to the effect of increased resistance at very low moisture content on the product of the grid current and resistance, when the glass electrode is used, for "with increased resistance a lower apparent pH is indicated." It is definitely shown that equilibrium values can be obtained for dry soils with the glass electrode, but it is extremely doubtful whether they are true pH values.

It is significant that in the pH studies on soils at low moisture contents, no recognition has been given to the fact that in making the pH determination at the moisture equivalent the soil is worked into a paste before the electrodes are inserted. Investigations in this laboratory (1, 5) have shown that the moisture equivalent is a critical point for soil puddling. In seven soils used in a study of puddling, 37 to 98 per cent of the moisture present at the moisture equivalent became bound when the soils were worked into a paste. Since bound water has

TABLE 2
Comparison of pH values, at the moisture equivalent, in puddled and unpuddled soils

SOIL NUMBER	PUDDLED	UNPUDDLED	PUDDLED*
	pH	pH	pH
C	8.85	8.80	8.80
2	7.90	7.75	7.85
3	7.75	7.70	7.80
4	7.50	7.65	7.60
5	7.70	7.55	7.60
7	9.05	9.05	9.05
8	7.85	7.70	7.80

* Values obtained after puddling the same soil portions used for determining the pH of unpuddled soils in column 3.

a reduced solvent power for salts and is less polar and less active, it is clear that the actual free water present in the soil paste is far less than that represented by the percentage of moisture in the soil at the moisture equivalent. In many cases the amount of free water present will approach that of an air-dry soil. The question naturally arises then: Is it necessary to attempt a measure of soil pH at moisture content below that of a soil paste. The following experiment will illustrate this.

Fifty-gram portions of soil, in two series, were weighed into 100-ml. beakers, and sufficient water was added to bring each to the moisture equivalent. One series was thoroughly puddled by working each into a paste. The other series was not worked into a paste but was allowed to stand for 24 hours in a water-saturated atmosphere so that the added water might come to equilibrium with the soil. On both series, pH determinations were made. As an additional check the unpuddled series was puddled after the pH determination in the unpuddled state had been completed. The pH values thus obtained are given in column 4 of table 2.

In comparison with the unpuddled soils, the pH was slightly higher in five of the puddled soils and slightly lower in one. In one soil the same pH value was obtained for all three determinations. In every case, however, the values may be considered well within the range of experimental error. This experiment indicates that no value should accrue from making pH determinations on soils at moisture contents below the moisture equivalent. Reduction in free water accomplished by puddling the soil is not accompanied by a reduction in pH.

SUMMARY

Comparative experiments show that determination of the pH value on a soil paste, at a moisture content approximating the moisture equivalent, accomplishes the same objective as that sought by Mattson in his pH of exchange neutrality and by Puri and Sarup in their isohydric pH. This agreement of the three methods tends to confirm the value of the paste method for determining the pH of any soil type.

REFERENCES

- (1) BUEHRER, T. F., AND ROSE, M. S. 1943 Studies in soil structure: V. Bound water in normal and puddled soils. *Ariz. Agr. Exp. Sta. Tech. Bul.* 100.
- (2) DAVIS, L. E. 1943 Measurements of pH with the glass electrode as affected by soil moisture. *Soil Sci.* 56: 405-422.
- (3) HEINTZE, S. C. 1934 The use of the glass electrode in soil reaction and oxidation-reduction potential measurements. *Jour. Agr. Sci.* 24: 28-41.
- (4) McGEORGE, W. T. 1937 The determination of soil reaction under field conditions by means of the spear type glass electrode. *Jour. Amer. Soc. Agron.* 29: 841-844.
- (5) McGEORGE, W. T. 1937 Studies in soil structure: II. Some characters of puddled soils. *Ariz. Agr. Exp. Sta. Tech. Bul.* 67.
- (6) MATTSON, S., AND WIKLANDER, L. 1940 The laws of soil colloidal behavior: XXIA. The amphoteric points, the pH, and the Donnan equilibrium. *Soil Sci.* 49: 109-152.
- (7) PURI, A. N., AND SARUP, A. 1938 Iso-hydric pH of soils and its determination. *Soil Sci.* 46: 49-56.

HYDROGEN-ION CONCENTRATION OF THE IMPORTANT SOILS OF THE UNITED STATES IN RELATION TO OTHER PROFILE CHARACTERISTICS: II. PEDALFERS AND SOILS TRANSITIONAL BETWEEN PEDOCALS AND PEDALFERS

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The hydrogen-ion concentration of the pedocals was discussed in a previous paper (1). The present paper, which deals with the pedalfers and the soils transitional between the pedocals and the pedalfers, considers only the most important series and the most representative profiles.

PEDALFERS

The pedalfers may be divided into two suborders: first, light-colored podzolized soils of the timbered regions, which include the podzols, brown podzolic soils, and gray-brown podzolic soils; and second, lateritic soils of the forested warm-temperature and tropical regions, which include the red and the yellow podzolic soils.

LIGHT-COLORED PODZOLIZED SOILS OF THE TIMBERED REGIONS

Podzols

Five series were selected to represent the podzols (21, 35, 44, 68) in the United States (1, fig. 1). They are the Au Train (72, 73), Roselawn (70, 71), Berkshire, Becket (38, 39, 40, 41), and Brassua (41).

Table 10 gives some of the morphological characteristics and the pH values of some of the more important types in these series.

The pH values of the solums of these profiles vary from 3.1 to 5.5 and those of their C horizons from 4.5 to 5.8 (table 10). These findings agree very closely with the data on profiles of this group reported by other investigators (4, 7, 11, 33, 45, 54, 57, 58, 67). The highest pH value of each profile usually occurs in the parent material. In their solums, the podzols average the most acid of the great soil groups. Six out of the ten profiles show the greatest acidity in the organic layer, two in the bleicherde, and one in the orterde. In many of the profiles there is little difference in acidity among the horizons of the solum.

The two series from the northern Great Lakes region are the Au Train and the Roselawn (table 10). The pH values of the Roselawn profiles range from 4.8 to 5.8, and those of the Au Train profiles, from 4.1 to 5.1. The solums of the Roselawn average less acid than those of the Au Train.

The three podzol series from New England have solums that average more acid than those from the northern Great Lakes region (table 10). This is doubt-

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TABLE 10

Podzols

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
96	<i>Au Train sand</i> Ontonagon Co., Mich.	4-0	A ₀ Organic. Blackish forest mold	4.1
		0-16	A ₂ Bleicherde. Pinkish gray loamy fine sand	5.1
		16-32	B ₂ Ortstein. Chocolate colored, fine sand cemented into an imperious hardpan	4.7
		32-60	C Parent material. Reddish brown fine sand—outwash plain	4.5
99	Alger Co., Mich.	3-0	A ₀ Organic. Leaf litter	4.1
		0-9	A ₂ Bleicherde. Gray loose sand	4.5
		9-60	B ₂ Ortstein. Dark brown sand cemented in places, becomes lighter in color and less cemented with depth	4.6
		72	C Pale yellow loose sand—outwash plain	5.0
101	<i>Roselawn sandy loam</i> Ogemaw Co., Mich.	2-0	A ₀ Organic. Finely divided organic matter, litter, and charred fragments	5.5
		0-2	A ₂ Bleicherde. Lavender-gray slightly loamy medium sand	5.0
		2-10	B ₂ Orterde. Brown gravelly sandy loam to light loamy sand	4.8
		10-30	B ₂₁ Orterde. Yellowish brown grading into grayish yellow. Slightly cemented in lower part	5.3
		30-40	C Parent material. Compact porous mottled brown and pale yellow gravelly sandy clay—glacial drift	5.8
102	Roscommon Co., Mich.	2-0	A ₀ Organic. Forest mold	5.5
		0-4	A ₂ Bleicherde. Gray leached sand	5.1
		4-11	B ₂ Orterde. Yellow-brown sandy gravelly loam	5.5
		11-34	B ₂ Yellow gravelly sand	5.5
		34-60	C Parent material. Reddish sand and gravelly clay mixture. Moderately pervious—glacial drift	5.3
103	<i>Berkshire loam</i> Vermont Recon.	2-0	A ₀ Organic. Dark brown forest debris	3.8
		0-1	A ₂ Bleicherde. Gray loam	3.8
		1-2	B ₂ Orterde. Dark brown loam	4.0
		2-16	B ₂₁ Orterde. Yellowish brown loam	4.5
		16-36	C Parent material. Pale yellowish brown glacial till	4.8

TABLE 10—Continued

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
105	<i>Berkshire loam—Cont'd</i> Hampshire Co., Mass.	2-0	A ₀ Organic. Forest debris	3.6
		0-2	A ₂ Bleicherde. Gray loam	4.0
		2-10	B ₂ Orterde. Yellow-brown loam	4.8
		10-22	B ₂ Greenish yellow loam	5.1
		22-48	C Parent material. Gray glacial till	5.2
106	<i>Becket loam</i> Berkshire Co., Mass.	6-0	A ₀ Organic. Dark brown leaf litter	4.0
		0-5	A ₂ Bleicherde. Gray friable loam	3.9
		5-18	B ₂ Orterde. Dark brown heavy loam	4.2
		18-30	C Greenish gray compact sandy clay, glacial till—considerable gravel	4.6
108	<i>Becket fine sandy loam</i> Berkshire Co., Mass.	2-0	A ₀ Organic. Raw humus	3.8
		0-1	A ₂ Bleicherde. Gray fine sandy loam	4.2
		1-2	B ₂ Orterde. Brown fine sandy loam	4.1
		2-18	B ₂₁ Orterde. Yellowish brown fine sandy loam	5.0
		18-22	C ₁ Greenish yellow fine sandy loam	5.1
		22-34	C ₂ Parent material. Greenish gray compact heavy glacial till	5.6
113	<i>Brassua fine sandy loam</i> Grafton Co., N. H.	3-0	A ₀ Organic. Partly disintegrated organic matter	3.8
		0-1	A ₁ Fairly well digested organic matter and sand	3.9
		1-5	A ₂ Bleicherde. Gray sand	4.0
		5-15	B ₂ Ortstein. Dark, rich brown fine sandy loam indurated in spots	4.8
		15-24	B ₂₁ Yellow-brown fine sandy loam	4.9
		24-32	B ₂ Pale yellow brown fine sandy loam grading to gray gritty clay loam	5.5
		32+	C Gray glacial till derived largely from granite	5.7
115	<i>Brassua sandy loam</i> Grafton Co., N. H.	10-5	A ₀₀ Organic. Brown undigested spruce needles	3.4
		5-0	A ₀ Organic. Forest black crumb mull	3.1
		0-3	A ₂ Bleicherde. Gray sandy loam	3.6
		3-4	B ₂ Ortstein. Rusty dark brown, slightly cemented sandy loam	3.7
		4-9	B ₂₁ Ortstein. Yellow-brown sandy loam, strongly cemented	4.5
		9-19	B ₂₂ Light yellowish brown to gray sandy loam, slightly cemented	4.6
		19+	C Gray glacial till	5.4

less due both to the higher rainfall in New England and to the difference in parent material. The parent material of the New England podzols is glacial till derived from schist, granite, and gneisses. The hydrogen-ion concentration of the Berkshire soils ranges from 3.6 to 5.2, that of the Becket from 3.8 to 5.6, and that of the Brassua from 3.1 to 5.7 (table 10). Of the podzols selected the Berkshire and the Brassua series have the most acid horizons. As in the case of the podzols from the northern Lake region derived from sandy material con-

TABLE 11
Brown podzolic soils

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
116	<i>Gloucester loam</i> Hampden Co., Mass.	0-2	A ₁ Dark brown fine sandy loam, high in organic matter	4.0
		2-6	B ₂ Dark brown loam	4.6
		6-12	B ₂₁ Deep brown or rusty brown loam	4.7
		12-20	B ₂₂ Yellow firm loam	4.8
		20-30	B ₃ Greenish yellow firm loam	4.8
		30-48	C Greenish yellow, slightly compact, cemented till	5.3
118	<i>Gloucester fine sandy loam</i> Berkshire Co., Mass.	3-0	A ₀ Dark leaf mold and organic matter	4.5
		0-2	B ₂ Brown fine sandy loam, high in organic matter	4.8
		2-12	B ₂₁ Yellowish brown fine sandy loam	5.0
		12-21	B ₂ Pale yellow fine sandy loam	5.2
		21-33	C Gray loose till	5.7
120	<i>Gloucester sandy loam</i> Norfolk Co., Mass.	1-0	A ₀ Partly decayed leaf litter	3.7
		0-2	B ₂ Coffee-brown sandy loam	4.1
		2-14	B ₂₁ Yellow-brown friable, firm sandy loam	4.5
		14-30	B ₂₂ Pale yellow-brown firm sandy loam	4.6
		30-40	C Gray gritty unaltered granitic till	4.6

taining no free carbonates, the most acid part of these soils is usually the organic layer, although the difference is slight in most cases.

Brown podzolic soils

Table 11 shows the pH of one of the important brown podzolic soil series as well as some of its morphological characteristics. The Gloucester series (37, 38, 39, 41) was selected to represent the brown podzolic soils (35, 44, 68) in the United States (1, fig. 1).

The pH values of the solums of these profiles range from 3.7 to 5.2 and those

of their C horizons from 4.6 to 5.7 (table 11). The solums average a trifle less acid than those of the New England podzols, especially in the upper layers (tables 10 and 11), and are of about the same acidity as those of the brown podzolic soils on the slopes of the Western Highlands of Scotland, as reported by Mitchell and Muir (47). In two of the three profiles, the parent material has a slightly higher pH value than any of the horizons in the solum. The solums of all three profiles show a slight tendency to decrease in acidity with depth. In general, the range from the most acid horizon in the solum to the C horizon is about 1.0 pH.

Gray-brown podzolic soils

Table 12 gives some of the profile characteristics and the hydrogen-ion concentrations of some of the more important gray-brown podzolic profiles (35, 44, 68; 1, fig. 1). Six series, the Sassafras, Collington, Chester, Hagerstown, Miami, and Clinton, were selected to represent this group.

The pH values of the solums of these profiles vary from 3.4 to 7.9 and those of their C and D horizons from 3.8 to 8.5. These are very similar to the data obtained by other investigators of this group (6, 11, 14, 15, 30, 32, 45, 54, 59, 65). As in the podzols, the high pH values occur usually in the parent material. Of the 12 profiles examined, four are neutral or alkaline in some part of the solum. Six profiles have surface layers that are neutral or very much less acid than the lower part of the solum. The solums of two are most acid in the B horizon, two profiles have the greatest acidity in the A₀ or A₁ horizon, one becomes more acid with depth, three are most acid in the lower A horizon, and one shows the greatest acidity in the lower A and upper B horizons.

The pH values of the Sassafras (10, 53) profiles range from 3.9 to 5.5 and those of the Collington (10, 53) profiles from 3.4 to 5.0.

Neither of the Chester (13, 74) profiles selected comes from an area that immediately adjoins the regions of podzols or brown podzolic soils. Consequently, neither shows the extreme acidity that the northern profiles of the Collington and Sassafras series do. The pH values of these profiles vary from 4.4 to 5.7 and average slightly higher than those of the Gloucester, Berkshire, Becket, and Brassua profiles (tables 10, 11, 12), which are all derived from somewhat similar parent materials. The Chester soils have formed on parent material residual from granite gneiss and mica schist, whereas the other four soils have formed on glacial till from granite, gneiss, and mica schist.

The pH values of the Hagerstown (29, 46) profiles vary from 4.5 to 7.4.

The pH values of the Miami (56, 69) profiles range from 5.0 to 8.5. These results vary considerably from the profile reactions of the Barnes series of the chernozem group, the Williams and the Scobey series of the chestnut group, and the Joplin series of the brown soils group, which have developed on nearly similar parent material but under less humid climates (1, tables 2, 3, 5; and table 12). The B₂ horizon of all three profiles is neutral or alkaline.

The parent material of the Clinton soils is similar to that of the Moody of the chernozem group and the Portneuf of the sierozem group (16, 20). The pH

values of these profiles varies from 5.4 to 8.2. This range appears very similar to that of the Miami, but the limy loess is much farther below the surface than

TABLE 12
Gray-brown podzolic soils

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
129	<i>Sassafras sandy loam</i> Camden area, N. J.	0- $\frac{1}{2}$	A ₁ Grayish black loamy sand	3.9
		$\frac{1}{2}$ -8	A ₂ Yellowish gray loamy sand	4.2
		8-15	A ₃ Yellow loamy sand	4.7
		15-30	B ₂ Yellowish red to reddish yellow light sandy clay	4.4
		30-60	C Reddish brown loamy sand	4.5
		60-80+	D Reddish yellow sand with occasional thin layers of fine sand	4.7
132	<i>Sassafras fine sandy loam</i> Anne Arundel Co., Md.	0-1	A ₁ Dark grayish brown friable fine sandy loam	5.5
		1-4	A ₂ Grayish brown friable fine sandy loam	4.3
		4-14	A ₃ Light yellowish brown friable fine sandy loam	4.7
		14-24	B ₁ Brown friable sandy clay loam	4.5
		24-38	B ₂ Reddish brown sandy clay, nut structure	4.5
		38-48	B ₂₁ Reddish brown sandy clay, nut structure	4.4
		48-72	C Mottled reddish brown, yellow, and gray alternate layers of fine silt loam, fine sandy loam and gravel	4.3
134	<i>Collington fine sandy loam</i> Anne Arundel Co., Md.	$\frac{1}{2}$ -0	A ₀ Dark grayish brown partly decomposed leaf litter	4.1
		0- $\frac{1}{2}$	A ₁ Dark brown friable fine sandy loam, high in organic matter	4.1
		$\frac{1}{2}$ -5	A ₂ Rich brown mellow fine sandy loam	4.5
		5-12	A ₃ Greenish brown heavy fine sandy loam	4.9
		12-20	B ₂ Dark greenish brown sticky sandy clay	5.0
		20-28	B ₂₁ Dark greenish brown heavy, sticky sandy clay	4.6
		28-37	B ₂₂ Dark greenish brown heavy, sticky fine sandy loam	4.7
		37-50	B ₃ Dull reddish plus olive-green heavy sticky fine sandy loam	4.7
		50-70	C Green sand	4.6

TABLE 12—Continued

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
136	<i>Collington loam</i> Camden area, N. J.	0-1	A ₁ Brownish black leaf mold and some loam soil	3.4
		1-8	A ₂ Grayish brown loam	4.4
		8-12	B ₁ Yellowish brown compact loam	4.5
		12-24	B ₂ Yellowish green compact clay	4.3
		24-46	C ₁ Greenish black sandy clay with some gravel	3.9
		46+	C ₂ Greenish black sandy clay with red and reddish brown mottlings	3.8
140	<i>Chester loam</i> Montgomery Co., Md.	$\frac{1}{2}$ -0	A ₀ Dark brown mull	5.2
		0- $\frac{1}{2}$	A ₁ Dark grayish brown loam high in organic matter	4.7
		$\frac{1}{2}$ -8	A ₂ Yellowish brown friable mellow loam	4.4
		8-30	B ₂ Reddish brown friable clay loam	5.1
		30-45	C ₁ Brownish yellow friable loam with considerable mica flakes	5.1
		45-54	C ₂ Mottled gray and reddish yellow, soft, partly decomposed rock—gneiss	5.2
141	Chester Co., Pa.	0-3	A ₁ Dark brown loam	5.7
		3-8	A ₂ Rich brown loam, a little lighter colored than A ₁	5.6
		8-38	B ₂ Yellow-brown clay loam	4.8
		38+	C Parent material—rotten granite	4.8
154	<i>Hagerstown silt loam</i> Washington Co., Ind.	0- $\frac{1}{2}$	A ₁ Dark grayish brown silt loam	7-4
		$\frac{1}{2}$ -1 $\frac{1}{2}$	A ₁₁ Very dark gray brown silt loam	7.2
		1 $\frac{1}{2}$ -4	A ₂ Brown silt loam	5.4
		4-13	A ₂₁ Brown silt loam, lighter colored than A ₂	5.0
		13-15	A ₃ Brown silt loam heavier than A ₂₁	5.1
		15-20	B ₁ Brown heavy silt loam	5.1
		20-26	B ₂ Brown silty clay loam	5.0
		26-30	B ₂₁ Light reddish brown silty clay loam heavier than B ₂	5.1
		30-39	B ₂₂ Reddish brown silty clay loam	5.2
		39-52	B ₂₃ Reddish brown silty clay loam, slightly redder than B ₂₂	5.0
		52-100	B ₃ Reddish brown silty clay loam, slightly redder than B ₂₃	5.0
		100-120	C ₁ Reddish brown silty clay, slightly redder than B ₃	5.2
		120-280	C ₂ Reddish brown silty clay with manganese stains	5.1
		280-296	C ₂₁ Light reddish yellow silty clay	7.0

TABLE 12—Continued

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
155	<i>Hagerstown silt loam—</i> Continued Franklin Co., Pa.	0-1	A ₁ Brownish gray granular silt loam high in organic matter	4.6
		1-5	A ₂ Brownish yellow mellow silt loam	4.8
		5-12	A ₃ Brown to reddish brown heavy silt loam	4.6
		16-20	B ₁ Reddish brown silty clay to clay	4.6
		20-30	B ₂ Reddish brown plastic clay loam, coarse angular nugget structure	4.6
		30-66	B ₃ Reddish brown plastic, brittle, non-granular clay	4.9
		66-80	C Reddish yellow-brown smooth plastic clay	4.5
159	<i>Miami silt loam</i> Hillsdale Co., Mich.	0-2	A ₁ Dark gray silt loam	5.3
		2-4	A ₂ Light gray silt loam	5.1
		4-10	A ₃ Grayish yellow gritty silt loam	5.3
		10-30	B ₂ Dark brown heavy gritty silt loam	7.9
		30+	C Dark brown and drab, slightly mottled, silty clay—glacial till	8.2
164	Rush Co., Ind.	0-2	A ₁ Dark brown silt loam	5.7
		2-12	A ₂ Brownish yellow silt loam	5.9
		12-20	B ₂ Yellowish brown to reddish brown silty clay loam	5.6
		20-28	B ₂₂ Brownish yellow to yellowish brown silty clay loam, streaked with gray	5.0
		28-32	B ₃ Streaked brown and brownish yellow silty clay loam, with small speckles of black	7.3
		32-45+	C ₁ Yellowish gray calcareous till, hard and gritty	8.5
172	<i>Clinton silt loam</i> Pierce Co., Wis.	0-4	A ₁ Dark grayish brown silt loam	6.9
		4-14	A ₂ Grayish yellow silt loam	5.4
		14-36	B ₁ Yellowish brown silty clay loam with white seams	5.4
		36-72	B ₂ Yellowish brown heavy silt loam	5.6
		72+	C Yellow friable silt loam	8.2
173	Trempealeau Co., Wis.	0-2	A ₁ Dark grayish brown silt loam	6.4
		2-9	A ₂ Light grayish brown silt loam	6.2
		9-36	B ₂ Light chocolate-brown crumbly silty clay loam	5.7
		36-72	C ₁ Light yellowish brown silt loam	6.4
		72-108	C ₂ Light yellowish brown silt loam	8.4
		108-180	C ₃ Grayish silt loam with rusty yellowish brown streaks, lime concretions	8.2

is the calcareous till of the Miami. In none of the profiles is the limy loess less than 6 feet from the surface.

LATERITIC SOILS OF THE FORESTED WARM-TEMPERATE AND TROPICAL REGIONS

The soils of the forested warm-temperate and tropical regions are represented in the United States by the two great soil groups, the red podzolic and the yellow podzolic (35, 44, 68). Five series, the Cecil, Davidson, Decatur, Orangeburg, and Blakely, were selected to represent the red podzolic soils and three, the Durham, Norfolk, and Tifton, to represent the yellow podzolic soils of the United States (1, fig. 1).

The yellow podzolic soils average slightly more acid than do the red podzolic soils (tables 13 and 14). The pH values of the yellow podzolic solums range from 4.0 to 6.1 and those of their C horizons from 4.6 to 5.2. The pH values of the red podzolic solums vary from 4.2 to 6.9 and those of their C horizons from 4.2 to 6.5. The figures are very similar to those reported by other investigators on red and yellow podzolic soils (7, 11, 30, 65) and are slightly lower than those obtained on red lateritic soils (5, 31, 64, 65). A third of the profiles of these two soil groups show a characteristic not exhibited to any degree by the other pedalfer soils so far studied: two of the six yellow podzolic profiles and three of the ten red podzolic profiles have C horizons more acid by 0.2 pH or more than the most acid horizons in the solum. This is undoubtedly due to the deep weathering caused by the high temperatures and heavy rainfall under which these two groups have developed. There is a strong tendency for both groups to have the same pH throughout their solums, although only two red podzolic profiles and one yellow podzolic profile actually have a variance of less than 0.2 pH between the horizons of their solums. The solums of six red podzolic profiles and two yellow podzolic become more acid with depth.

Red podzolic soils

Table 13 gives some of the morphological characteristics and the pH values of some of the more important of the red podzolic soils.

The pH values of the profiles of both solum and parent material of the Cecil series (26, 42) range from 5.0 to 6.0. The solum of one profile has the same hydrogen-ion concentration throughout.

The pH values of the profiles of the Davidson (28, 34) and Decatur series (18, 61) vary from 4.2 to 6.6. The higher pH values, in comparison with the Cecil soils, are undoubtedly due to the fact that the parent materials of the Davidson and Decatur soils are higher in bases. The solums of one of the Davidson profiles and of both the Decatur profiles become more acid with depth, and that of one Davidson profile has virtually the same pH throughout.

The pH values of the Orangeburg (27, 48) soils range from 4.5 to 6.2. The solums of both profiles become more acid with depth.

The pH values of Blakeley (12, 43) profiles range from 5.0 to 6.9. This series is the least acid of the red podzolic soils. One profile becomes more acid with depth and the other shows a very slight tendency to become less acid with depth.

TABLE 13
Red podzolic soils

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
191	<i>Cecil sandy loam</i> Greenwood Co., S. C.	0-1	A ₁ Dark grayish brown friable sandy loam high in organic matter	5.5
		1-8	A ₂ Light brown mellow sandy loam	6.0
		8-30	B ₁ Red stiff but brittle clay, which breaks into irregular lumps	5.6
		30-84	B ₂ Yellowish red friable clay, containing some sand and mica mottled with yellow	5.2
		84+	C Light gray disintegrated granite, mottled with yellow and brown	5.0
194	<i>Cecil fine sandy loam</i> Caswell Co., N. C.	0-2	A ₁ Dark gray sandy loam high in organic matter	5.2
		2-9	A ₂ Brownish yellow mellow sandy loam	5.2
		9-45	B ₂ Red stiff but brittle clay containing a small amount of mica	5.2
		45-90	B ₂₁ Light red stiff brittle clay, with mottlings of yellow; not quite so heavy as B ₂	5.2
		90-150	C ₁ Light red and yellow sandy clay with considerable mica and pieces of rotten granite	5.2
		150-270	C ₂ Light red and yellow friable partly decomposed granite	5.2
199	<i>Davidson clay loam</i> Orange Co., Va.	0-4	A Reddish brown clay loam	5.7
		4-30	B ₁ Deep red, very friable, finely granular clay, with manganese aggregates	5.0
		30-96	B ₂ Deep red, friable, porous, finely granular clay	4.8
		96-144	C ₁ Yellow sticky residual clay and rotten rock	4.2
		144+	C ₂ Raw diabase, very hard greenish to bluish fine crystalline basic rock lava	4.7
201	Rockingham Co., N. C.	0-1	A ₁ Dark brown leaf mold	4.6
		1-5	A ₂ Reddish brown clay loam, friable, crumbly	4.5
		5-48	B ₂ Deep red or maroon-red heavy stiff clay	4.5
		48-66	C ₁ Light red with particles of yellow ochreous friable clay	4.5
		66	C ₂ Yellow soft rotten rock with black streaks and green specks	4.5

TABLE 13—Continued

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
204	<i>Decatur clay loam</i> Franklin Co., Ala.	0-3	A ₁ Dark reddish brown clay loam	6.6
		3-8	A ₂ Reddish brown clay loam	5.8
		8-48	B ₂ Deep red heavy clay	5.8
		48-72	B ₂₁ Red clay, friable and crumbly	4.6
		72+	C Mottled and streaked reddish brown and yellow compact but friable clay	4.7
205	Bartow Co., Ga.	0-2	A ₁ Dark red loam	5.2
		2-7	A ₂ Red clay loam	4.5
		7-84	B ₂ Dark red heavy clay	4.2
		84-100	C Mottled red and yellow clayey material	4.2
212	<i>Orangeburg fine sandy loam</i> Nacogdoches Co., Tex.	0-4	A ₁ Slightly dark yellowish gray loamy fine sand	6.1
		4-12	A ₂ Yellowish gray fine sandy loam	6.2
		12-36	B ₂ Red friable sandy clay	4.9
		120	C Dull red sandy clay	4.5
216	<i>Orangeburg sandy loam</i> Lee County, Ga.	0-6	A ₁ Dark gray loose sand high in organic matter	4.9
		6-18	A ₂ Grayish yellow loose, friable sandy loam—some organic matter	4.8
		18-60	B ₂ Bright red, rather light and friable sandy clay	4.8
		60-80	B ₂₁ Red sandy clay, friable, brittle, with few streaks and blotches of yellow	4.5
		80-144	C Compact brittle, friable sandy clay mottled with gray, yellow, red, and rusty brown	4.5
221	<i>Blakely clay loam</i> Early Co., Ga.	0-1½	A ₁ Dark reddish brown loam	6.9
		1½-7	A ₂ Reddish brown friable clay loam	5.4
		7-20	B ₂ Reddish brown friable clay	5.3
		20-45	B ₂₁ Maroon-red, heavy, stiff, smooth clay	5.0
		45-60	C Mottled grayish white, yellow, reddish, and purplish, stiff, brittle sandy clay	5.1

TABLE 13—*Continued*

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
224	<i>Blakely loam</i> Dougherty Co., Ga.	$\frac{1}{2}$ –0	A ₀ Dark brown leaf mold	5.7
		0–2 $\frac{1}{2}$	A ₁ Brownish black heavy sandy loam	5.7
		2 $\frac{1}{2}$ –7	A ₂ Dark brown loam	5.6
		7–12	B ₁ Dark reddish brown light but sticky sandy clay	5.8
		12–16	B ₂ Dark reddish brown sticky sandy clay	6.0
		16–20	B ₂₁ Reddish brown sticky sandy clay, spongy structure	6.1
		20–24	B ₂₂ Reddish brown sticky sandy clay, spongy structure	6.1
		24–32	B ₂₃ Heavy reddish brown sticky sandy clay	6.4
		32–36	B ₂₄ Heavy reddish brown sticky sandy clay	6.4
		36–40	B ₂₅ Heavy reddish brown sticky sandy clay	6.4
		40–44	B ₃ Reddish brown friable sandy clay	6.4
		44–48	C Coarsely mottled red and brown friable sandy clay	6.5

Yellow podzolic soils

Table 14 gives some of the morphological characteristics and the pH values of some of the more important yellow podzolic soils.

The pH values of Durham (19, 42) soils vary from 4.0 to 6.1. The average is slightly more acid than that of the Cecil profiles (tables 13 and 14), which have developed on similar parent material. This might indicate that the flatter topography and consequent greater hydration of the iron compounds have a tendency to increase the acidity of the profile. One of the profiles becomes more acid with depth.

The pH values of the Norfolk and Tifton (9, 63, 75) profiles are very similar, though those of the Tifton average slightly less acid. The pH values of the Norfolk profiles range from 4.4 to 5.0 and those of the Tifton from 4.5 to 5.8. These values are similar to those of the Durham, but the Norfolk profiles are a trifle more acid than the Orangeburg profiles, which have developed on similar parent material (tables 13 and 14). The solum of one Norfolk profile becomes more acid with depth and the solum of the other Norfolk profile has the same pH throughout. The two Tifton profiles are most irregular as to which horizon is most acid. The C horizon of one profile is the most acid.

SOILS TRANSITIONAL BETWEEN THE PEDOCALS AND THE PEDALFERS

The selected soils in the United States that are transitional between the pedocals and the pedalfers belong to three great soil groups: noncalcareous brown, prairie, and reddish prairie soils.

TABLE 14
Yellow podzolic soils

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
240	<i>Durham sandy loam</i> Hart Co., Ga.	0-1	A ₁ Dark gray sandy loam	4.0
		1-12	A ₂ Pale yellow light sandy loam	4.7
		12-28	B ₂ Yellow brittle friable clay	4.6
		28-44	B ₂₁ Streaked light red, gray and yellow sandy clay	4.8
		44-54	C Reddish yellow and yellow friable material	4.8
242	Greenwood Co., S. C.	0-5	A ₁ Gray loamy coarse sand, some organic matter	6.1
		5-20	A ₂ Pale yellow loamy coarse sand	5.0
		20-40	B ₂ Yellow coarse sandy clay	4.8
		40-56	B ₃ Heavy clay, with yellow light gray and reddish brown mottlings	4.8
		56-70	C Purplish red, yellow and light gray rotten granite	4.6
247	<i>Norfolk fine sandy loam</i> Harrison Co., Miss.	0-3	A ₁ Light brown loamy fine sand	5.0
		3-5	A ₂ Brownish yellow fine sand to fine sandy loam	5.0
		5-16	A ₃ Yellow fine sandy loam	4.7
		16-30	B ₂ Yellow heavy fine sandy loam	4.7
		30-52	B ₂₁ Yellow heavy fine sandy loam to fine sandy clay loam	4.4
		52-70	C Yellow friable fine sandy clay, mottled red, reddish yellow, yellowish red and gray	4.4
		70-88	D ₁ Compact fine sandy clay, splotted bright red, bluish gray, reddish yellow and purplish red	4.4
		88-100	D ₂ Fine sandy loam variegated bluish gray, bright yellow and red	4.6
		100-114	D ₃ Fine sandy clay slightly compact, splotted deep red, reddish yellow bluish gray and yellow	4.6
		114-126	D ₄ Compact fine sandy loam, containing some gravel and chert	4.6
		126-132	D ₅ Light bluish gray fine sandy clay	4.6
		132-140	D ₆ Bluish gray sandy clay splotted with red and bright yellow	4.6
		140-146	D ₇ Bluish gray fine sandy clay mottled with yellow, reddish yellow and red	4.7
		146-160	D ₈ Fine sandy clay splotted red bluish gray, bright red and yellow	4.7

TABLE 14—*Continued*

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
250	<i>Norfolk sandy loam</i> Houston Co., Ala.	0-6	A ₁ Gray loamy sand	4.9
		6-10	A ₂ Pale yellow loamy sand	4.9
		10-23	A ₃ Light yellowish brown friable light sandy loam	4.9
		23-37	B ₂ Yellow friable sandy clay	4.9
		37-49	B ₂₁ Yellow slightly mottled with reddish brown crumbly sandy clay	4.9
		49-80	C Imperfectly weathered sandy clay mottled light gray, brown and red	4.9
255	<i>Tifton sandy loam</i> Irwin Co., Ga.	0-2	A ₁ Grayish brown loamy sand, containing dark brown iron pebbles	5.1
		2-10	A ₂ Pale yellowish brown loamy sand containing dark brown iron pebbles	5.5
		10-22	B ₂ Bright yellow friable sandy clay with a high proportion of iron pebbles	5.1
		22-36	B ₂₁ Bright reddish yellow friable sandy clay, high proportion of iron pebbles	5.2
		36-54	C ₁ Compact but friable sandy clay mottled light gray, yellow and rust-brown	5.2
		54-70	C ₂ Compact but friable sandy clay mottled light gray, yellow, rust-brown and purple	5.2
257	Toombs Co., Ga.	0-1½	A ₁ Very dark gray loamy sand high in organic matter	5.8
		1½-2½	A ₁₁ Grayish brown loamy sand with many brown concretions	5.2
		2½-14	A ₂ Brownish yellow loamy sand	5.6
		14-25	B ₁ Yellowish brown sandy loam	5.8
		25-55	B ₂ Light yellowish brown, friable sandy clay	4.9
		55-80	C Mottled brownish yellow and reddish brown and purplish brown friable sandy clay	4.5

Noncalci brown soils

Table 15 shows some of the morphological characteristics and the pH values of three profiles of the Sierra (60) series, selected to represent the noncalci brown soils (55; 65; 66; 68; 1, fig. 1).

The pH values of the profiles range from 5.9 to 6.6. These average very much less acid than those of the pedalfer soils developed on similar parent rock, such as the Cecil, Durham, Chester, Gloucester, Becket, and Brassua series (tables 10, 11, 12, 13 and 14), but more acid than the data reported by Thorp and Tshan on the Shantung brown soils (65, 68). One of the Sierra profiles is most acid in the A₂ horizon, one is most acid in the B₁ horizon, and the third becomes less acid with depth. The C horizons of two profiles have virtually the same

TABLE 15
Noncalcic brown soils

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
260	<i>Sierra loam</i> Placerville area, Cal.	0-2	A ₁ Light reddish brown loam, fine granular structure	6.5
		2-14	A ₂ Reddish brown friable granular loam	6.0
		14-28	B ₂ Red compact clay, nut structure	6.2
		28-60	B ₂₁ Deep red compact clay, jointed structure	6.4
		60+	C Decomposed granite	6.4
261	<i>Sierra clay loam</i> Placerville area, Cal.	0-1½	A ₁ Reddish brown granular loam, platy structure when dry	6.2
		1½-8	B ₁ Red clay loam	6.0
		8-14	B ₂ Red compact gritty clay, jointed structure	6.2
		14-28	B ₂ Red very compact gritty clay, prismatic structure	6.5
		28+	C Decomposed granite	6.2
262	<i>Sierra clay</i> Placerville area, Cal.	0-8	A ₁ Brownish red somewhat compact clay, nut structure	5.9
		8-15	B ₂ Red compact cloddy clay	6.1
		15-28	B ₂₁ Deep red very compact clay, jointed structure	6.2
		28+	C Decomposed granite	6.6

hydrogen-ion concentrations as the respective solums, and that of the other profile has a slightly higher pH than any horizon in the solum.

Prairie soils

Table 16 shows some of the profile characteristics and the pH values of the more important prairie (35, 44, 68) soils. Four series, the Clarion, Marshall, Carrington, and Tama, were selected to represent this group (1, fig. 1).

The pH values of the solums of these profiles range from 5.0 to 8.1 and those of the C horizons from 5.6 to 8.5. These average slightly more acid than those

of the chernozem profiles (table 2) but considerably less acid than those of the gray-brown podzolic profiles and slightly less acid than those of the noncalcareous brown profiles (tables 12 and 15). The solums of five of the eight profiles studied have the lowest pH in the lower A and upper B horizons. In each of five of the profiles, the uppermost horizon has a higher pH than the layer immediately below.

The pH values of the Clarion (50, 51) profiles range from 5.8 to 8.3. These results are similar to those reported by Norton and Bray (49). They are virtually the same as those of the Barnes (table 2) but average considerably higher than those of the Miami (table 12). These three series have all developed on similar parent materials.

The pH values of the Marshall (2, 25) profiles vary from 5.2 to 8.5. The average is a trifle more acid than that of the Clarion and the Moody (table 2) and considerably less acid than that of the Clinton series (table 12). The Moody, Clinton, and Marshall have all formed on similar parent materials.

The pH values of the Carrington (3, 52) profiles vary from 5.1 to 6.7. The average is considerably less than that of the Clarion profiles. The Carrington series differs from the gray-brown podzolic Miami in having the C horizon acid to mildly alkaline instead of alkaline (tables 2 and 12).

The Tama series has developed on loess similar to the parent material of the Marshall and that of the gray-brown podzolic Clinton series (52). As it occurs in a more humid climate than the Marshall, the parent loess is leached of its lime to a depth of 5 or more feet. The pH values of the Tama profiles range from 5.0 to 6.5. These values are very similar to those of the Carrington but average a trifle lower. The Tama profiles average considerably more acid than those of the Marshall. The solums average less acid than those of the gray-brown podzolic Clinton, developed on similar parent material (table 12).

Reddish prairie soils

Table 17 shows some of the morphological characteristics and the pH values of some of the more important reddish prairie soils (1, fig. 1). Three series, the Renfrow, Pond Creek (8, 17, 22, 23), and Newtonia (36, 62), were selected to represent the Reddish prairie soils (68). The pH values of the solums of these profiles vary from 4.7 to 7.9; those of their C horizons from 5.0 to 7.8. These results are similar to those of the prairie soils but a trifle lower (table 16). Harper (24) in Oklahoma reports very similar reactions on profiles of two of the series of reddish prairie soils. The solums of three of the six profiles become gradually less acid with depth; that of one shows the greatest acidity in the lower A and upper B horizons; and those of two become more acid with depth. Only two profiles have a higher pH at the surface than immediately below, and in each the difference is very slight.

The Newtonia profiles have the lowest pH values of the three series studied. They range from 4.7 to 6.6. Their C horizons are more or less acid. One is even very strongly acid at a depth of 60 to 72 inches. The other two series in this group have virtually the same pH range in their profiles, from 5.4 to 7.9.

TABLE 16
Prairie soils

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
263	<i>Clarion loam</i> Carroll Co., Iowa	0-2	A ₁ Dark brown loam	7.1
		2-12	A ₂ Dark grayish brown mellow loam	6.4
		12-20	B ₂ Yellowish brown fine sandy clay loam, few dark streaks of organic matter	6.3
		20-50	C ₁ Pale yellow friable silty clay loam—glacial till	8.3
		50-70	C ₂ Mottled dark gray and yellowish brown silty clay—glacial till	8.1
		70-90	C ₃ Pale yellow brown silty material streaked with gray and dark brown—glacial till	8.2
264	Pocahontas Co., Iowa	0-3	A ₁ Dark grayish brown loam	7.4
		3-12	A ₂ Very dark grayish brown loam	5.8
		12-33	A ₃ Dark grayish brown loam	5.8
		33-37	B ₂ Yellowish brown clay loam	8.1
		37-57	C Yellowish brown silty clay loam splotted with lime aggregates and iron stains—glacial till	8.1
268	<i>Marshall silt loam</i> Harrison Co., Iowa	0-5	A ₁ Very dark grayish brown silt loam	7.5
		5-15	A ₂ Very dark grayish brown heavy silt loam	7.5
		15-25	B ₁ Dark grayish brown silt loam	7.6
		25-34	B ₂ Dark grayish brown silt loam, slightly lighter in color	7.4
		34-42	B ₃ Grayish brown mellow silt loam	5.2
		42-47	C ₁ Grayish yellow silt loam—loess	7.4
		47-53	C ₂ Grayish yellow calcareous loessial silts	8.0
		53-60	C ₃ Yellow calcareous loessial silts	8.1
270	Boone Co., Nebr.	0-2	A ₁ Very dark grayish brown, friable, granular silt loam filled with grass roots	7.2
		2-8	A ₂ Very dark grayish brown, friable, granular silt loam	6.9
		8-16	A ₃ Dark grayish brown friable silt loam, less granular than A ₂	6.1
		16-26	B ₁ Brown, faintly granular, friable silt loam with organic matter streaks	6.2
		26-38	B ₂ Brown, heavy silt loam that breaks into soft clods	6.7

TABLE 16—Continued

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
	<i>Marshall silt loam—Con.</i>			
		38-45	B ₂ Light brown calcareous silty clay loam that breaks into soft clods	7.1
		45-58	C ₁ Brownish yellow calcareous loessial silt	8.2
		58-98	C ₂ Grayish yellow calcareous loessial silt	8.3
		98-118	C ₂ Light gray calcareous loessial silt	8.5
	<i>Carrington loam</i>			
275	Buchanan Co., Iowa	0-3	A ₁ Dark grayish brown, smooth, friable loam full of grass roots	5.4
		3-9	A ₂ Very dark grayish brown mellow loam	5.1
		9-16	B ₁ Dark grayish brown to grayish brown heavy loam to light silty clay loam	5.1
		16-24	B ₂ Brown silty clay loam	5.1
		24-32	B ₂ Yellowish brown silty clay loam	5.8
		32-54	C ₁ Yellowish brown silty clay loam containing considerable coarse sand and some fine gravel—glacial till	6.7
		54-70	C ₂ Yellowish brown silty clay loam to clay loam, gritty—glacial till	6.7
	<i>Carrington silt loam</i>			
276	Guthrie Co., Iowa	0-2	A ₁ Dark grayish brown smooth silt loam full of grass roots	6.1
		2-14	A ₂ Almost black, mellow, friable silt loam	5.6
		14-30	B ₂ Dark yellowish brown, friable heavy silt loam to silty clay loam	5.9
		30-60	C ₁ Yellowish, brown silty clay loam faintly mottled with gray and rust-brown, more friable than B ₂ —glacial till	6.1
		60-72	C ₂ Yellowish brown gravelly clay loam mottled with gray and rust-brown—glacial till, noncalcareous	6.0
	<i>Tama silt loam</i>			
278	Knox Co., Ill.	0-6	A ₁ Dark grayish brown friable, finely granular silt loam	5.0
		6-10	A ₂ Very dark grayish brown friable, finely granular silt loam	5.4
		10-13	A ₂₁ Dark grayish brown, friable, finely granular silt loam, slightly lighter in color than A ₂	5.3

TABLE 16—Continued

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
	<i>Tama silt loam—Cont'd</i>			
		13-18	A ₁ Dark grayish brown, friable, finely granular silt loam, slightly lighter in color than A ₂₁	5.1
		18-29	B ₁ Dark grayish brown, friable, heavy silt loam to silty clay loam, some granulation	5.2
		29-35	B ₂ Brown silty clay loam, heavier than B ₁ ; breaks into soft clods	5.3
		35-41	B ₂ Yellowish brown silty clay loam; breaks into soft clods	5.5
		41-53	C ₁ Mottled gray and brown silt loam to silty loam, lighter textured and more friable than B ₂	5.7
		53-61	C ₂ Yellow friable silt loam—loess	5.8
		61-71	C ₂ Lighter yellow friable silt loam—loess	5.9
		71-86	C ₄ Lighter yellow friable silt loam—loess	6.2
279	Guthrie Co., Iowa	0-3	A ₁ Dark grayish brown silt loam, friable and granular	6.4
		3-9	A ₂ Very dark grayish brown friable silt loam, very granular	6.5
		9-16	A ₃ Dark grayish brown friable silt loam, not so granular as A ₂	5.3
		16-23	B ₁ Grayish brown to light brown friable silt loam	5.2
		23-35	B ₂ Yellowish brown friable heavy silt loam; falls apart into soft clods	5.3
		35-46	C ₁ Pale yellowish brown friable silt loam streaked with dark colors—loess	5.6
		46-65	C ₂ Mottled gray brown and rust brown structureless silt loam—loess	5.8
		65-78	C ₂ Brown structureless silt loam less mottled than above horizon—loess	6.2

Their C horizons are neutral to mildly alkaline. A comparison of the pH values of the Newtonia with the other two series clearly shows the effect of climate on hydrogen-ion concentration of the soil profiles. As an illustration, the Newtonia profile from Lawrence County, Missouri, which is the most acid of the group studied, has developed considerably east of the reddish prairie area in a region with a mean temperature of 56°F. and an average annual rainfall of 46 inches, whereas the Renfrow and Ponk Creek series have developed under a

TABLE 17
Reddish prairie soils

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
288	<i>Renfrow silt loam</i> Garfield Co., Okla.	0-6	A Reddish brown to chocolate-brown silt loam	6.4
		6-10	B ₁ Reddish brown silty clay loam	6.4
		10-22	B ₂ Brownish red to red clay; breaks into shiny surface granules	6.6
		22-30	C Brownish red dense clay	6.7
		30-36+	D Reddish brown noncalcareous shale of Permian red beds—parent rock	7.1
290	Grant Co., Okla.	0-7	A Dark reddish brown silt loam	5.7
		7-18	B ₁ Reddish brown clay loam	5.6
		18-36	B ₂ Reddish brown heavy clay	6.0
		36-60	B ₃ Reddish brown clay	7.9
		60-72	C Red clay	7.8
293	<i>Newtonia silty clay loam</i> Doniphan Co., Kans.	0-6	A Dark reddish brown silt loam to silty clay loam	6.5
		6-10	B ₁ Light brown to faint reddish brown silty clay loam	6.6
		10-34	B ₂ Reddish brown silty clay to clay with little gray mottling, considerable iron concretions, and dark brown stains	5.5
		34-60	C Grayish brown clay mottled about half and half with brown and light brown and olive-gray	6.3
294	<i>Newtonia silt loam</i> Lawrence Co., Mo.	0-7	A ₁ Dark reddish brown silt loam	6.2
		7-12	A ₂ Slightly reddish brown silt loam	5.6
		12-18	B ₁ Reddish brown silty clay loam	5.4
		18-24	B ₂ Reddish brown clay loam	5.2
		24-30	B ₂₁ Dull red clay loam	5.2
		30-36	B ₂₂ Dull red friable clay loam	4.9
		36-60	B ₃ Red clay	4.7
		60-72	C Red clay mottled with gray	5.0
299	<i>Pond Creek silt loam</i> Alfalfa Co., Okla.	0-6	A Dark reddish brown silt loam	6.0
		6-24	B ₁ Dark brown silt loam, prismatic structure	6.1
		24-42	B ₂ Reddish brown friable silt loam	6.3
		42-72	B ₃ Dark reddish brown silty clay loam, cubical structured horizon	6.3
		72-80	C Reddish brown calcareous silt loam	7.5

TABLE 17—*Continued*

PROFILE NUMBER	LOCATION	DEPTH	DESCRIPTION OF HORIZON	pH
		<i>inches</i>		
300	Major Co., Okla.	0-1½	A ₁ Dark reddish brown silt loam	6.3
		1½-6	A ₂ Dark reddish brown heavy silt loam	6.1
		6-12	A ₃ Reddish brown heavy silt loam	5.9
		12-22	B ₁ Light reddish brown silt loam	5.8
		22-36	B ₂ Dark red heavy silty clay loam	6.0
		36-58	B ₂₁ Dark reddish brown heavy clay	6.8
		58-64	B ₃ Red clay	7.1
		64-72	C Red calcareous clay	7.6

mean temperature of 58 to 59°F. and an annual rainfall of 29 to 31 inches. The other Newtonia profile studied has developed under intermediate climatic conditions and, therefore, has intermediate pH values. The parent limestone and dolomite of this series certainly should contain as high a content of calcium carbonate as the limy parent shales and sandstone of the other series of this group; therefore, the lower pH values of these profiles cannot be due to parent material.

SUMMARY

All of the pedalfer profiles (light-colored podzolic soils of the timbered regions and lateritic soils of forested warm-temperate regions) show a strong tendency to have more or less acid solums. They range from extremely acid to mildly alkaline in the B₃ horizons.

The podzols and brown podzolic soils have the most acid solums, their pH ranging from 3.1 to 5.8. The general tendency is for the organic matter horizons of the solum to be the most acid.

The solums of the gray-brown podzolic, red podzolic, and yellow podzolic profiles have a very similar pH range. The solums of the gray-brown podzolic group range from 3.4 to 7.9, those of the red podzolic soils from 4.2 to 6.9, and those of the yellow podzolic soils from 4.0 to 6.1. The profile reactions of these three groups are most variable.

There is no uniformity in the gray-brown podzolic soils as to which horizon of the solum will be most acid.

One-third of the yellow and the red podzolic profiles studied are more acid in the C horizon than in any part of the solum.

There is a strong general tendency for the red and the yellow podzolic soils to have the same pH throughout their solums.

Over half of the red podzolic solums and one third of the yellow podzolic solums become more acid with depth.

The transitional soils, represented by the noncalcic brown, prairie, and reddish prairie soils, are intermediate in reaction between the pedocals and the pedalferes. Their solums vary from very strongly acid to strongly alkaline.

The solums of the noncalcic brown soils range from medium acid to slightly acid.

The pH values of the profiles of the prairie soils range from 5.0 to 8.5, and those of the reddish prairie soils range from 4.7 to 7.9.

Five eights of the solums of the prairie soils are most acid in the lower A and upper B horizons.

Half of the solums of the reddish prairie soils become less acid and one third more acid with depth.

REFERENCES

- (1) BAILEY, E. H. 1944 Hydrogen-ion concentration of the soils of the United States in relation to other profile characteristics: 1. Pedocal soils. *Soil Sci.* 57: 443-474.
- (2) BENTON, T. H., AND RUSSELL, N. J. 1928 Soil survey of Harrison County, Iowa. *U. S. Bur. Chem. and Soils Field Oper.* 1923: 823-858.
- (3) BENTON, T. H., et al. 1931 Soil survey of Buchanan County, Iowa. *U. S. Bur. Chem. and Soils, Soil Surveys, Ser.* 1926, No. 33.
- (4) BJØRLYKKE, K. O. 1928 Soil types and soil profiles in Norway. *Proc. and Papers First Internatl. Cong. Soil Sci.* 4: 223-269.
- (5) BONNET, J. A. 1939 The nature of laterization as revealed by chemical, physical, and mineralogical studies of a lateritic soil profile from Puerto Rico. *Soil Sci.* 48: 25-40.
- (6) BRAY, R. H., AND DETURK, E. E. 1932 Chemical aspects of some Illinois soils as related to their genesis and morphology. *Proc. and Papers Second Internatl. Cong. Soil Sci.* (1930) 5: 118-131.
- (7) BROWN, I. C., AND BYERS, H. G. 1938 Chemical and physical properties of certain soils developed from granitic materials in New England and the Piedmont and of their colloids. *U. S. Dept. Agr. Tech. Bul.* 609.
- (8) BUCKHANNAN, W. H., et al. 1940 Soil survey of Major County, Oklahoma. *U. S. Bur. Plant Industry, Soil Surveys, Ser.* 1936, No. 2.
- (9) BURKE, R. T. A., AND SWEET, A. T. 1925 Soil Survey of Houston County, Alabama. *U. S. Bur. Soils Field Oper.* 1920, *Rpt.* 22: 315-344.
- (10) BURKE, R. T. A., AND LEE, L. L. 1931 Soil survey of the Camden area, New Jersey. *U. S. Bur. Chem. and Soils, Soil Surveys, Ser.* 1926, No. 28.
- (11) BYERS, H. G., ALEXANDER, L. T., AND HOLMES, R. S. 1935 The composition and constitution of the colloids of certain of the great groups of soils. *U. S. Dept. Agr. Tech. Bul.* 484.
- (12) CARR, M. E., et al. 1916 Soil survey of Dougherty County, Georgia *U. S. Bur. Soils Field Oper.* 1912, *Rpt.* 14: 573-631.
- (13) CARTER, W. T., AND HULL, J. P. D. 1919 Soil survey of Montgomery County, Maryland. *U. S. Bur. Soils Field Oper.* 1914, *Rpt.* 16: 393-427.
- (14) CONREY, G. W. 1933 Genesis and morphology of the gray-brown forest soils of the eastern United States. *Rpt. Ann. Meeting Amer. Soil Survey Assoc.* 13: 32-39.
- (15) CONREY, W. W., AND GREEN, T. C. 1932 Relation of state of development of soils to their degree of base saturation. *Amer. Soil Survey Bul.* 13: 111-125.
- (16) EDWARDS, M. J., et al. 1932 Soil survey of Trempealeau County, Wisconsin. *U. S. Bur. Chem. and Soils, Soil Surveys, Ser.* 1927, No. 35.
- (17) FITZPATRICK, E. G., et al. 1939 Soil survey of Garfield County, Oklahoma. *U. S. Bur. Chem. and Soils, Soil Surveys Ser.* 1935, No. 6.
- (18) FULLER, G. L., AND SHORES, H. H. 1930 Soil survey of Barton County, Georgia. *U. S. Bur. Chem. and Soils, Soil Surveys, Ser.* 1926, No. 11.
- (19) FULLER, G. L. 1933 Soil survey of Hart County, Georgia. *U. S. Bur. Chem. and Soils, Soil Surveys, Ser.* 1929, No. 12.
- (20) GEIB, W. J., et al. 1929 Soil survey of Pierce County, Wisconsin. *U. S. Bur. Chem. and Soils, Soil Surveys, Ser.* 1923, No. 43: 1471-1504.

- (21) GLINKA, K. D. 1914 Die Typen der Bodenbildung, ihre Klassifikation und geographische Verbreitung. Berlin.
- (22) GOKE, A. W., AND HOLLOPETER, C. A. 1935 Soil survey of Grant County, Oklahoma. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1931, No. 10.
- (23) GOKE, A. W., et al. 1939 Soil survey of Alfalfa County, Oklahoma. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1933, No. 23.
- (24) HARPER, H. J. 1937 Factors which affect the development of prismatic structure in soils of the southern great plains. *Proc. Soil Sci. Soc. Amer.* 2: 447-453.
- (25) HAYES, F. A., AND MORTLOCK, H. C. 1926 Soil survey of Boone County, Nebraska. *U. S. Bur. Soils Field Oper.* 1921, *Rpt.* 23: 1169-1220.
- (26) HEARN, W. E., AND DRANE, F. P. 1911 Soil survey of Caswell County, North Carolina. *U. S. Bur. Soils Field Oper.* 1908, *Rpt.* 10: 317-340.
- (27) HENDRICKSON, B. H., DEVEREUX, R. E., AND TEMPLIN, E. H. 1930 Soil survey of Nacogdochis County, Texas. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1925, No. 24.
- (28) HENDRICKSON, B. H. 1930 Soil survey of Orange County, Virginia. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1927, No. 6.
- (29) HIGBEE, H. W., et al. 1938 Soil survey of Franklin County, Pennsylvania. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1931, No. 31.
- (30) HOLMES, R. S., AND EDGINGTON, G. 1930 Variations of the colloidal material extracted from the soils of the Miami, Chester, and Cecil series. U. S. Dept. Agr. Tech. Bul. 229.
- (31) HORNBY, A. J. W. 1932 Reaction of horizons in tropical soils. *Nature* 129: 58.
- (32) JEFFRIES, C. D., AND WHITE, J. W. 1937 Some mineralogical and chemical characteristics of a Hagerstown soil profile. *Proc. Soil Sci. Soc. Amer.* 2: 133-141.
- (33) JENNY, H. 1927 Soil investigations of the Swiss Alps. *Proc. and Papers First Internat. Cong. Soil Sci.* 4: 421-428.
- (34) JURNEY, R. C., AND DAVIS, W. A. 1930 Soil survey of Rockingham County, North Carolina. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1926, No. 7.
- (35) KELLOGG, C. E. 1936 Development and significance of the great soil groups of the United States. U. S. Dept. Agr. Misc. Pub. 229.
- (36) KNOBEL, E. W., et al. 1931 Soil survey of Doniphan County, Kansas. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1927, No. 25.
- (37) LATIMER, W. J., et al. 1925 Soil survey of Norfolk, Bristol, and Barnstable Counties, Massachusetts. *U. S. Bur. Soils Field Oper.* 1920, *Rpt.* 22: 1033-1120.
- (38) LATIMER, W. J., AND LANPHEAR, M. O. 1929 Soil survey of Berkshire County, Massachusetts. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1923, No. 39; 1267-1313.
- (39) LATIMER, W. J., AND SMITH, L. R. 1932 Soil survey of Hampden Hampshire Counties, Massachusetts. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1928, No. 25.
- (40) LATIMER, W. J., et al. 1937 Soil survey (reconnaissance) of Vermont. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1930, No. 43.
- (41) LATIMER, W. J., et al. 1939 Soil survey of Grafton County, New Hampshire. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1935, No. 6.
- (42) LESH, F. R., et al. 1934 Soil survey of Greenwood County, South Carolina. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1929, No. 26.
- (43) LONG, D. D., AND HALL, E. C. 1924 Soil survey of Early County, Georgia. *U. S. Bur. Soils Field Oper.* 1918, *Rpt.* 20: 419-457.
- (44) MARBUT, C. F. 1935 Soils of the United States. Atlas of American Agriculture, Part III. U. S. Dept. Agr., Washington, D. C.
- (45) MATTSO, S., AND GUSTAFSSON, Y. 1934 Chemical characteristics of soil profiles: I. The podzol. *Ann. Agr. Col. Sweden* 1: 33-69.
- (46) MILLER, J. F., et al. 1939 Soil survey of Washington County, Indiana. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1932, No. 36.
- (47) MITCHELL, R. L., AND MUIR, A. 1935 The brown earth in Scotland, its relation to continental types. *Trans. Third Internat. Cong. Soil Sci.* 1: 322-323.

- (48) MOON, J. W. 1930 Soil survey of Lee County, Georgia. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1927, No. 4.
- (49) NORTON, E. A., AND BRAY, R. H. 1929 The soil reaction profile. *Jour. Amer. Soc. Agron.* 21: 834-844.
- (50) O'NEAL, A. M., AND DEVEREUX, R. E. 1930 Soil survey of Carroll County, Iowa. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1926, No. 5.
- (51) O'NEAL, A. M., AND DEVEREUX, R. E. 1932 Soil survey of Pocahontas County, Iowa. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1928, No. 19.
- (52) ORRBN, C. L., et al. 1933 Soil survey of Guthrie County, Iowa. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1929, No. 15.
- (53) PHILLIPS, S. W., et al. 1932 Soil survey of Anne Arundel County, Maryland. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1928, No. 18.
- (54) RADU, I. F. 1933 Die Veränderung des Reaktions Zustandes des Bodens deren Grundflagen. *Landw. Vers. Sta.* 116: 267-322.
- (55) SHAW, C. F. 1928 Soil profile development and the relationship of soils in California. *Proc. and Papers First Internatl. Cong. Soil Sci.* 4: 291-317.
- (56) SIMMONS, C. S., et al. 1937 Soil survey of Rush County, Indiana. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1930, No. 44.
- (57) SMOLIK, I. F. 1928 Principal soil profiles in Czechoslovakia. *Proc. and Papers First Internatl. Cong. Soil Sci.* 4: 323-327.
- (58) STEBUTT, A. 1930 Lehrbuch der allgemeinen Bodenkunde. Berlin.
- (59) STEVENSON, R. E. 1927 Reaction profile studies. *Proc. and Papers First Internatl. Cong. Soil Sci.* 4: 383-390.
- (60) STORIE, R. E., AND TRUSSELL, D. F. 1931 Soil Survey of the Placerville area, California. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1927, No. 34.
- (61) STROUD, J. E., et al. 1931 Soil survey of Franklin County, Alabama. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1927, No. 30.
- (62) SWEET, A. T., AND JORDAN, H. V. 1928 Soil survey of Lawrence County, Missouri. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1923, No. 34: 1123-1159.
- (63) TAYLOR, A. E., et al. 1939 Soil survey of Toombs County, Georgia. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1935, No. 11.
- (64) THORP, J. 1935 Geographic distribution of the important soils of China. *Bul. Geol. Survey China* 14 (2).
- (65) THORP, J. 1936 Geography of the Soils of China. Natl. Geol. Survey China.
- (66) THORP, J., AND TSHAN, T. Y. 1936 Notes on Shantung soils. Natl. Geol. Survey China. Soil Bul. 14.
- (67) TILL, A. 1933 Ortsbodentypen. *Soil Res.* 2: 163-195.
- (68) United States Department of Agriculture 1938 Yearbook *Soils and Men*. Washington, D. C.
- (69) VEATCH, J. O., et al. 1928 Soil survey of Hillsdale County, Michigan. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1924, No. 10.
- (70) VEATCH, J. O., SCHOENMANN, L. R., AND FULLER, G. L. 1928 Soil survey of Ogemaw County, Michigan. *U. S. Bur. Soils Field Oper.* 1923: 903-928.
- (71) VEATCH, J. O., SCHOENMANN, L. R., AND MOON, J. W. 1929 Soil survey of Roscommon County, Michigan. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1924, No. 27.
- (72) VEATCH, J. O., et al. 1934 Soil survey of Alger County, Michigan. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1929, No. 32.
- (73) VEATCH, J. O., SCHOENMANN, L. R., AND SHEARIN, A. E. 1935 Soil survey of Luce County, Michigan. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1924, No. 38.
- (74) WILDER, H. J., et al. 1907 Soil survey of Chester County, Pennsylvania. *U. S. Bur. Soils Field Oper.* 1905, Rpt. 7: 135-174.
- (75) WILDERMUTH, R., et al. 1928 Soil survey of Harrison County, Mississippi. U. S. Bur. Chem. and Soils, Soil Surveys, Ser. 1924, No. 7.

BOOKS

Historical Geology. By RUSSELL C. HUSSEY. McGraw-Hill Book Company, Inc., New York, 1944. Pp. 491, figs. 344. Price, \$3.50.

To compress into fewer than 500 pages the geologic history of the earth, which, as measured by the extent of the disintegration of uranium into lead and helium, has been in existence some 2,000,000,000 years, is difficult, but the author of this book has succeeded in doing it in a very admirable manner. The text, supported by many excellent illustrations, gives one a glimpse of long-past happenings such as would stimulate the imagination of the uninitiated and would serve to renew the appreciation of those who need to review this exciting subject. Anyone who wants to know more about the earth will find something of interest and value on every page. Incidentally, the word "soil" is not shown in the index.

Root Disease Fungi. By S. D. GARRETT. The Chronica Botanica Company; G. E. Stechert and Company, New York, 1944. Pp. 177, figs. 9. Price, \$4.50.

This book is of more than usual interest to those having to do with soil management in relation to crop production in that it deals with one of the more obscure phases of this problem about which there is great need for more exact information than has been contained in the usual classroom textbook. The first eight chapters deal with the nature and activities of root-infecting fungi and the effects of the temperature, moisture, texture, reaction, and organic matter of the soil upon them. The last seven chapters have to do with methods of control. Of the control procedures, crop rotation, plant sanitation, and a considerable variety of other possibilities are discussed. The suggestions touched upon in the sections on "accelerating natural disappearance of parasites from the soil" and "use of organic supplements" need to be expanded, but this will have to wait until this field of study has been more fully explored.

A Shorter History of Science. By WILLIAM CECIL DAMPIER. The Macmillan Company, New York City, 1944. Pp. 189, figs. 14, plates 9. Price, \$2.

This is a worthy attempt to bring together in concise form the progress of science from the dawn of history forward. The several chapters deal with The Origins, Rome and Greece, The Middle Ages, The Renaissance, Galileo and Newton, The First Physical Synthesis, The Eighteenth Century, Physics and Chemistry of the Nineteenth Century, Nineteenth-Century Biology, Recent Biology, The New Physics and Chemistry, and The Stellar Universe. The objective is to present to "older schoolboys," a term which probably includes most of us, a comprehensive picture of "man's attempts to understand the mysterious world in which he finds himself" and to emphasize the need to avoid overspecialization.

Soil and Plant Analysis. By C. S. PIPER. Interscience Publishers, Inc., New York, 1944. Pp. 368, figs. 17. Price, \$4.50.

This is a photo offset reprint of the book reviewed in *Soil Science*, page 68, volume 56. The methods included are those in use in the laboratories of the Waite Agricultural Research Institute of the University of Adelaide in Australia.

The Soil Science Society of Florida Proceedings. Volume 3. Third Annual Meeting of the Society, Gainesville, December 4-5, 1941. The Soil Science Society of Florida, R. V. Allison, Sec.-Treas, Gainesville. Pp. 145. Price, \$1.

This delayed report includes the papers presented at the spring meeting at Orlando on a practical grouping of Florida soils, soil reaction, substituted cations in the soil complex, nitrogen sources for citrus, and cover crops for vegetables. The papers presented at the winter meeting had to do with citrus culture, characteristics of tropical rubber soils, English-Spanish soil equivalents, organic matter in Florida soils, copper adsorption, turbidimetric determination of potassium, and a symposium on pasture management. Two of the papers are published both in English and in Spanish as a move in the direction of improved relationships with the Latin-American nations, a function of the Institute of Inter-American affairs, which was organized at the University of Florida in 1930.

THE EDITORS.

IONIC REACTIONS IN SOILS AND CLAY SUSPENSIONS: THE SIGNIFICANCE OF SOIL FILTRATES

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THE CONCEPT OF THE OSCILLATION VOLUME OF AN ION

The nature of the forces which bind adsorbed ions to the surfaces of soil or clay particles has been the subject of much speculation. Since the discovery of the crystalline nature of clay colloids, however, it is generally conceded that these forces must be electrostatic in character. This conclusion is in harmony with the electrical properties of soil and clay suspensions. Moreover, the electrical as well as the base-exchange properties of soils indicate that the adsorbed ions are not rigidly held on the surface. If the colloidal clay surface is assumed to be characterized by discrete attraction spots, an adsorbed ion might be expected to occupy an infinite number of possible positions about a particular attraction spot. In effect, these positions would describe a three-dimensional zone about the attraction spot in which the adsorbed ion might be expected to oscillate. This picture of the adsorbed ions was assumed by Jenny in the development of a kinetic theory of base exchange (9). Jenny's concept of the electric double layer is in no apparent conflict with the idea of the diffuse ion swarm of Gouy (7) and Debye and Hückel (4) and in addition it includes cases where the attraction spots may be far apart.

DESCRIPTION OF CERTAIN COLLOID PHENOMENA IN TERMS OF THE OSCILLATION VOLUME CONCEPT

On the basis of the foregoing picture of the clay surface, it has been possible to visualize a number of phenomena which might be expected to occur in soil and colloidal clay systems.

The first of these phenomena is attendant on the condition that the surface attraction spots are sufficiently close together that the oscillation zones of the adsorbed ions overlap. This situation would enable individual adsorbed ions to migrate over the entire colloidal surface by a process of exchange. This process has been called the *surface migration of ions* (10).

A second phenomenon might be expected to result from collision between colloidal particles. At the close approach of two colloidal particles certain oscillation zones of the particles would be expected to intermingle. This condition would enable the transfer of adsorbed ions from one particle to another by a process of exchange. This process has been discussed in previous papers under the heading of *contact exchange of ions* (10).

On the same basis, a further property of soil and clay systems has been antici-

¹ Division of Soils. The author is indebted to H. Jenny and L. E. Davis for suggestions and criticism.

pated and experimentally investigated (10). This property concerns the effective concentration of ions at a fixed surface within a colloidal clay suspension. Because of the continual encounter of the surface with the oscillation zones of the bombarding particles, it would be expected that the mean concentration of ions at any given fixed surface in a suspension would be greater than that in the intermicellar liquid or filtrate of the suspension. Thus it would not be inconsistent with the picture to find that the chemical potentials of cations in some soils are higher than in a sample of the intermicellar liquid or soil solution with which the soil might be in equilibrium. That this is actually the case is attested by a number of experimental facts, some of long standing.

THE SUSPENSION EFFECT; THE CONTACT EFFECT

Rice and Osugi in 1918 (12) noticed that the pH values of certain soil suspensions were measurably lower than those of the filtrates and centrifugates. This observation was later verified by Bradfield (1) and by Wiegner (13). This phenomenon, insofar as it involves the hydrogen ion, has come to be known as the *suspension effect*, a term initiated by Wiegner. In recent years Jenny and Overstreet (10) have demonstrated that certain effects of cations on plant roots and on mineral and metallic surfaces occur readily in clay suspensions but to a much less extent in the corresponding filtrates or centrifugates. Jenny and Overstreet have selected the term *contact effect* to describe these general phenomena.

Since the time of Wiegner, a lively controversy has appeared in the literature concerning the interpretation of the suspension effect and even in regard to the validity of the observations themselves. These discussions recently were reviewed by Davis.² In the writer's opinion, the suspension effect and the contact effect are manifestations of the same phenomenon, and theoretical objections to the one apply equally well to the other. For this reason, and because of the important implications of the effects in the field of soil science, an attempt will be made here to point out that these effects are in harmony with well-established theory and are to be expected.

CONDITIONS FOR EQUILIBRIUM BETWEEN CLAY SUSPENSIONS AND ELECTROLYTE SOLUTIONS

For the better visualization of the problem, let us consider a system comprising two phases in equilibrium (fig. 1). Let the first phase (A) be an aqueous suspension of colloidal clay which may contain some free electrolytes, and let the second phase (B) be a water solution. We shall assume that the boundary is impermeable to the clay particles and permeable to all other ions present. Moreover, we shall assume that phase A is a clay suspension or gel which is near its swelling maximum; that is, there is no appreciable tendency for water to move from one phase to another. Then, for the purpose of the theory, the interface is equivalent to a membrane which is impermeable to the clay particles and to the solvent molecules but permeable to all other particles. Phase B might be identified with

² Davis, L. E. Donnan equilibria and suspension effects in colloidal clay systems. 1941. [Unpublished doctor's thesis. Univ. Calif., Berkeley.]

the filtrate obtained by the slow filtration of a very large amount of the clay suspension. The system just postulated may be classified as a "Donnan system," and the equilibrium attained may be called a "Donnan equilibrium." In the present discussion, however, we shall deal with certain more general relationships of equilibrium than those derived by Donnan (5) and by Donnan and Guggenheim (6). This procedure seems appropriate because clay suspensions are far from ideal solutions and our present information concerning the activities of anions and cations in colloids of this type is meager. Systems involving membranes with the assumed restraints are treated in standard texts on physical chemistry and chemical thermodynamics (2, 8, 11). A brief summary of the theory is presented here.

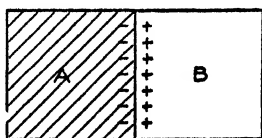


FIG. 1

Because the membrane is impermeable to the clay anions, there will be a separation of electric charge in the region of the boundary between the two phases; that is, an electric double layer will be set up. An electrical field will be set up normal to the surface between the phases. Since electrical work is required to carry a unit charge across a double layer, a potential difference is thus established between the phases. Potential differences of this type have been widely discussed under such headings as boundary potentials, liquid-liquid junction potentials, and membrane potentials.

In general, interface potential differences cannot be measured with the same degree of precision as can the electromotive forces of certain electrolytic cells. Nonetheless, in many cases their magnitudes can be determined with a fair degree of assurance. Brønsted (2) points out that a membrane potential is measurable as the difference between the electromotive potentials of two standard electrodes (*e.g.*, calomel electrodes) in contact with the solutions on the two sides of the membrane, the junction potential being eliminated. For the present, we shall examine the consequences of such a potential difference on thermodynamic reasoning. We shall assume that phase A is at an electrical potential ψ_A , and phase B is at a potential ψ_B .

Most thermodynamic relationships governing equilibria occurring at constant temperature, pressure, and electric potential can be derived from the equation

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (1)$$

where G is the Gibbs free energy (Lewis' F), S the entropy, T the absolute temperature, V the volume, P the pressure, n_i the number of mols of the chemical species i , and μ_i the chemical potential of the species i . In systems at constant temperature, pressure, and electric potential, μ_i is identical with the partial molal

free energy (\bar{F}_i) of Lewis and Randall.³ Equation (1) tells us that the conditions for equilibrium at constant T , P , and ψ are

$$dG = 0 \quad \text{or} \quad \sum_i \mu_i dn_i = 0 \quad (2)$$

This means that the chemical potential μ_i of the molecular species i must have the same value at all points in the equilibrium system. Equation (2) is applicable to charged ions as well as to neutral molecules.

In the case of systems (such as that represented in figure 1) which contain phases at different electric potentials, we may still apply the foregoing thermodynamic equations in regard to the diffusible ions. Instead of the chemical potential, μ_i , however, we must substitute the electrochemical potential $\bar{\mu}_i$. Thus at constant T and P , the condition for equilibrium in systems of this type is

$$\sum_i \bar{\mu}_i dn_i = 0 \quad (3)$$

or in other words, $\bar{\mu}_i$ must be invariant. The electrochemical potential, $\bar{\mu}_i$, may be thought of as consisting of two parts, one purely chemical, μ_i , and the other purely electrical $z_i F\psi$, where z_i is the valence of the ion species, i , and F is Faraday's number. Thus we may write

$$\bar{\mu}_i = \mu_i + z_i F \psi \quad (4)$$

From equation (3) we may conclude that for any number of phases in equilibrium, all of which may be at different electric potentials, the electrochemical potential of any diffusible ion must be the same throughout the system. This being true, it follows from equation (4) that for a system of phases at different electrical potentials the *chemical potential* must vary from one phase to another. For the clay system postulated above

$$(\bar{\mu}_i)_A = (\bar{\mu}_i)_B$$

but

$$(\mu_i)_A \neq (\mu_i)_B$$

for any diffusible ion. Also from (3) and (4):

$$(\mu_i)_A + z_i F \psi_A = (\mu_i)_B + z_i F \psi_B$$

or

$$(\mu_i)_A - (\mu_i)_B = z_i F (\psi_B - \psi_A) \quad (5)$$

The quantity $(\psi_B - \psi_A)$ is the interface potential. The above thermodynamic equations state formally that a difference in chemical potential for ions in the clay suspension and in the filtrate is concomitant with a potential difference between the two phases.

To summarize, the existence of an interface potential between a soil suspension

³ In nonideal solutions μ_i is related to molal activity, a_i , by the equation

$$\mu_i = RT \ln a_i + k_i$$

where k_i is a constant which is determined by the pressure and temperature of the system.

and its filtrate, or any electrolyte phase with which it is in equilibrium, leads to the conclusion on thermodynamic reasoning that the chemical potential of any diffusible ion is different in the two phases. This being true, one must expect that chemical equilibria involving a given diffusible ion also must be different in the two phases⁴.

CONCLUSIONS REGARDING THE CONTACT EFFECT AND THE SUSPENSION EFFECT

As previously implied, interface potentials cannot be measured by rigid thermodynamic methods, although their magnitudes often can be measured approximately. Interface potentials between clay suspensions and electrolyte solutions recently have been studied by Davis (3). The boundary potential was measured as the difference between the electromotive potentials of two calomel electrodes, one electrode being connected to the clay suspension by means of a saturated KCl salt bridge and the other connected to the electrolyte solution by means of a saturated KCl bridge. For negative clay suspensions, the filtrate was found to be at a higher electrical potential than the suspension. That is, for clay suspensions, the quantity $(\psi_B - \psi_A)$ of equation (5) is positive. Davis allowed suspensions of sodium bentonite to come to equilibrium with solutions of NaCl in membrane cells. Subsequent determination of the interface potentials showed a marked inverse relationship between the potential and the concentration of the NaCl solution. For example, a bentonite suspension (containing 6.87 gm. Na-bentonite per liter) in equilibrium with a solution containing 0.00024 mol per liter of NaCl gave an interface potential of 7.0 millivolts, and a similar suspension (also containing 6.87 gm. Na-bentonite per liter) in equilibrium with a solution containing 0.0107 mol per liter of NaCl gave a potential of 0.6 millivolt. In general it was found that for fixed concentrations of clay the greatest potential differences between suspensions and their equilibrium filtrates were produced in systems containing little or no free electrolytes; that is, systems in which the ion swarms about the clay particles were diffuse. Systems containing an excess of free electrolytes (ion swarms repressed) showed small potential differences.

These observations, together with the relationship of equation (5), permit a further elucidation of the contact effect and of the suspension effect. Since the potential difference $(\psi_B - \psi_A)$ is positive for clay suspensions, it follows from equation (5) that for any diffusible cation

$$(\mu_i)_A > (\mu_i)_B.$$

This inequality of chemical potentials will be the greater the smaller the amount of free salts present (diffuse ion-swarms about the particles). For suspensions containing an excess of free electrolytes, the interface potential $(\psi_B - \psi_A)$ and consequently the difference in chemical potentials will be small. On the basis of this reasoning, contact effects and suspension effects will be most noticeable in soils containing little or no free electrolytes and they will be in the direction of higher chemical potentials for cations in the suspension than in the filtrate. On the assumption that the absorption of a cation by plant roots depends on the chemical

⁴ This statement of course does not apply to equilibria involving the transfer of ions from one phase to another.

potential of the ion at the root surface, it may be anticipated that cations will be more readily absorbed from the suspension than from the corresponding filtrate in many soil-water systems. Also, since the pH determination is very probably a measure of the chemical potential of H^+ ion, the suspension would be expected to have a lower pH than the filtrate.

The foregoing line of reasoning leads to some interesting conclusions regarding the anions in clay suspensions containing small amounts of free electrolytes. Since z_i is negative for anions, equation (5) leads to the result that for all diffusible anions

$$(\mu_i)_A < (\mu_i)_B.$$

Since the chemical potential of any anion is less in the suspension than in the corresponding filtrate, plant roots might be expected to absorb anions less readily from some soil suspensions than from the filtrates.

In conclusion, it may be said from the foregoing analysis that the contact effect and the suspension effect are at least theoretically to be expected with all clay or soil suspensions. Moreover, because of the inequalities in the chemical potentials of the diffusible ions, an examination of the soil solution in many cases will not give a correct picture of the chemical properties of the corresponding soil suspension. From what is known of the properties of the ionic double layer and interface potentials in clays, these conclusions are particularly applicable to systems in which the free electrolyte concentration is low.

REFERENCES

- (1) BRADFIELD, R. 1924 Effect of the concentration of colloidal clay upon its hydrogen-ion concentration. *Jour. Phys. Chem.* 28: 170-175.
- (2) BRÖNSTED, J. N. 1938 Physical Chemistry. Chemical Publishing Company, New York.
- (3) DAVIS, L. E. 1942 Significance of Donnan equilibria for soil colloidal systems. *Soil Sci.* 54: 199-219.
- (4) DEBYE, P., AND HÜCKEL, E. 1923 Zur Theorie der Electrolyte. *Phys. Ztschr.* 24: 185-206; 305-325.
- (5) DONNAN, F. G. 1911 Theorie der Membrangleichgewichte und Membranpotentiale bei Vorhandensein von nicht dialysierenden Elektrolyten. *Ztschr. Elektrochem.* 17: 572-581.
- (6) DONNAN, F. G., AND GUGGENHEIM, E. A. 1932 Die genaue Thermodynamik der Membrangleichgewichte. *Ztschr. Phys. Chem. (A)* 162: 346-360.
- (7) GOUY, M. 1910 Sur la constitution de la charge électrique à la surface d'un electrolyte. *Jour. Phys.* 9: 457-468.
- (8) GUGGENHEIM, E. A. 1932 Modern Thermodynamics by the Methods of Willard Gibbs. Methuen and Company, London.
- (9) JENNY, H. 1936 A simple kinetic theory of ionic exchange. *Jour. Phys. Chem.* 40: 501-517.
- (10) JENNY, H., AND OVERSTREET, R. 1939 Surface migration of ions and contact exchange. *Jour. Phys. Chem.* 43: 1185-1196.
- (11) MACDOUGALL, F. H. 1939 Thermodynamics and Chemistry. John Wiley and Sons, Inc., New York.
- (12) RICE, F. E., AND OSUGI, S. 1918 Inversion of cane sugar by soils and allied substances and the nature of soil acidity. *Soil Sci.* 5: 333-358.
- (13) WIEGNER, G. 1931 Some physical chemical properties of clays: II. Hydrogen clay. *Jour. Soc. Chem. Indus.* 50: 103-112.

BASE-EXCHANGE-pH RELATIONSHIPS IN SEMIARID SOILS

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The property of a soil to respond to changes in environment has prompted such statements as that there is no such thing as a true base-exchange capacity or a true soil pH value. As one reviews the literature the confusion of data and opinions more or less supports these declarations. Despite the dynamic character of these two soil values, they are intimately related, however, in semiarid soils. Gedroiz, Kelley, and others have shown that the exchange complex may be a major source of alkalinity in soils. It is true that the base-adsorption capacity of a soil is no longer considered a constant, for it is now known to increase with increase in the pH of the salt solution in contact with the soil. As for the pH value, it is also true that soil minerals hydrolyze when in contact with water and therefore the pH of the soil varies with the soil:water ratio. The experiments of Kelley and Brown (2) and Tiulin and Bystrova (6), which showed an increase in base adsorption on treatment of the soils with $\text{Ca}(\text{OH})_2$, and those of Bradfield (1) with KCl solution made alkaline with KOH are in harmony with the above. Likewise it has been shown in this laboratory (3) that the amount of adsorbed sodium in black alkali soils is greater than the total base-adsorbing capacity as determined with neutral $N \text{ NH}_4\text{C}_2\text{H}_3\text{O}_2$. The relation between pH and base-adsorption capacity is further emphasized by Mattson and Hester (4), who stress the essentiality of stating the pH at which the adsorption capacity is determined. Puri and Uppal (5) have suggested that adsorption capacity be expressed in the form of a titration curve from which the base-adsorbing capacity can be determined at any pH. In view of this changeable base-adsorption capacity the question naturally arises as to the effect of this on the active and potential alkalinity of the soil and the pH determination.

RELATION BETWEEN pH AND ADSORBED SODIUM

The total adsorption capacity and adsorbed sodium were determined on a selected group of saline and alkaline soils, and the ratio between these two values was calculated. The data are given in figure 1 where the ratio of adsorbed Na to total adsorption capacity is plotted against the pH values of the soils. The relationship is linear. The correlation between the pH of the soil paste and the ratio is highly significant, and the 1:10 soil:water ratio shows a significant correlation. The linear relation is one of increase in pH with increase in percentage of exchange capacity that is satisfied with sodium. The data show that there is very definitely a relation between pH and adsorbed sodium when the sodium is expressed on a percentage basis.

RELATION BETWEEN pH AND ABSOLUTE AMOUNTS OF ADSORBED SODIUM

Semiarid soils vary in adsorbing capacity from about 4 m.e. per 100 gm. of soil in sands to 40 m.e. per 100 gm. in clays. Obviously when a sand is com-

pletely saturated with sodium it will contain less sodium, on an absolute weight basis, than a clay which is only partly saturated with sodium. In view of the linear relation between the pH and the ratio of adsorbed sodium to adsorbing capacity, and in view of the wide variation in adsorption capacity in soils of varying texture, the next experiment was designed to determine the relation between pH and the absolute amount of adsorbed sodium in the soil.

For this experiment a group of 10 soils was selected with adsorption capacities varying from 3.7 m.e. per 100 gm. (sandy soil) to 23.7 m.e. per 100 gm. (a soil containing 40 per cent clay). In order to place these soils on a comparable basis and at the same time eliminate salinity effects, portions of each soil were saturated with sodium. This was accomplished by leaching the soils with a normal solution of NaCl adjusted to pH 9.5 with NaOH. The excess of NaCl was removed by washing the soil once with distilled water and then with 60 per

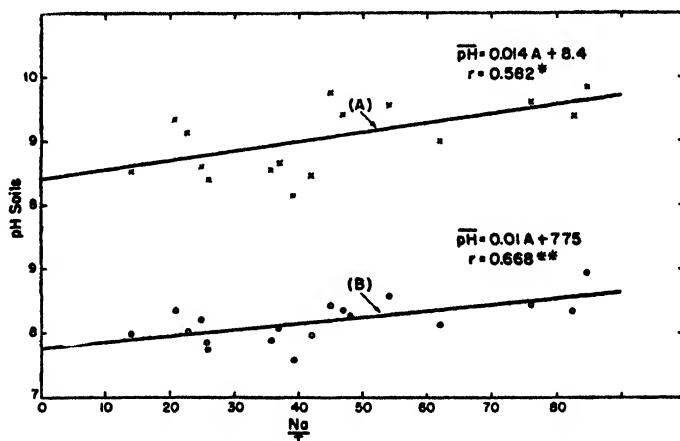


FIG. 1. RELATION BETWEEN pH OF SOILS AND RATIO OF ADSORBED Na TO TOTAL ADSORPTION CAPACITY, Na/T

cent methanol until free from chloride. The soils were then dried in the air and their pH values determined at 1:10 soil:water ratio and, on the soil paste, at approximately the moisture equivalent. Both values were determined in order to bring out the hydrolytic pH exhibited by the soil on dilution and represented by the difference between these two pH values. The analytical data are given in figure 2.

The data show that regardless of the adsorption capacity of the soil, the pH values for all at 1:10 soil:water ratio are approximately the same. This means that all alkaline-calcareous soils, when saturated with sodium and when neutral salts are absent, will exhibit nearly the same hydrolytic pH at 1:10 ratio regardless of the absolute amount (as milliequivalents per 100 gm.) of adsorbed sodium present. In actual figures the sandy soil with an adsorbing capacity of 3.7 m.e. per 100 gm. has the same high pH as the clay loam with an adsorbing capacity of 23.7 m.e. When the pH values are determined on the soil paste there is a highly significant decrease in pH with increase in milliequivalents adsorbed

sodium per 100 gm. That is, the pH is lowest for the soils containing the most adsorbed sodium.

These data are interpreted to mean that the soils containing the most silt and clay, and having the highest adsorbing capacity, are strongly buffered by the greater colloid content and therefore at field moisture content have a lower pH value than sandy soils with lower adsorbing and buffer capacities. When the pH of the soil paste is subtracted from the pH of the 1:10 soil:water ratio (A, fig. 2), to show the effect of dilution on pH, there is a highly significant increase in this difference with increase in milliequivalents adsorbed sodium. This means that the clay soils possess the greatest potential alkalinity and exhibit the

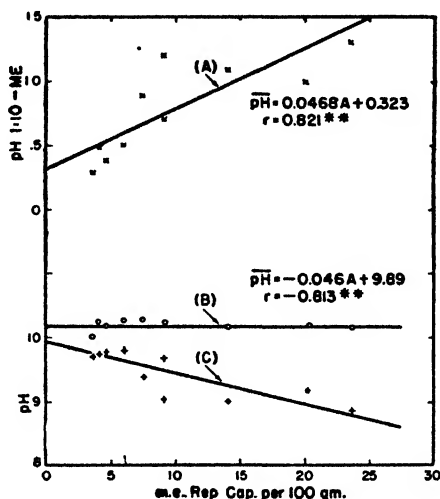


FIG. 2. RELATION BETWEEN pH AND MILLIEQUIVALENTS Na PER 100 GM. SOIL IN Na-SATURATED SOILS

C, pH at moisture equivalent; B, pH at 1:10 soil:water ratio; A, difference between these two pH values. ME = moisture equivalent; Rep. Cap. = adsorption capacity.

greatest hydrolytic pH. These data show that crops should be able to withstand higher pH values in sandy soils than in clay soils or even silts. Because the sandy soils contain less potential alkalinity, and lower buffer capacity, they should offer less resistance to the reduction in pH of the root-soil contact film which results from root respiration.

EFFECT OF INCREASED BASE ADSORPTION AT HIGH pH VALUES ON FINAL pH OF SOIL

The next experiment was designed to study the effect of the increased base adsorption obtained by treating soils with salt solutions of high pH value on the pH of the soil.

The purpose of the first experiment was to determine definitely the effect of salt solutions of high pH on the adsorption capacity of alkaline-calcareous soils. Five-gram portions of six soils were leached first with 250 ml. of *N* NaCl solution

which had been adjusted to pH 11.1 with NaOH, then with 60 per cent methanol until free from chloride, and finally with 250 ml. of $N \text{ NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution adjusted to pH 8.5. Sodium was determined in the leachate and NH_4 determined in the soil, by distillation, after the excess salt had been washed out with 60 per

TABLE 1

Comparison of adsorption capacity of alkaline-calcareous soil as determined with neutral normal ammonium acetate, sodium chloride at pH 11.1, and ammonium acetate pH 8.5

SOIL NUMBER	, ADSORPTION CAPACITY OF SOIL		
	Ammonium acetate, pH 7.0	NaCl, pH 11.1	Ammonium acetate, pH 8.5
	<i>m.e. NH₄</i>	<i>m.e. Na</i>	<i>m.e. NH₄</i>
4	7.4	13.6	10.6
8	20.3	23.4	25.5
3	9.2	14.5	12.0
7	9.2	14.8	14.0
6	4.7	6.7	5.0
2	14.0	19.2	20.1

TABLE 2

pH values of soils after saturation with Na from sodium acetate solutions at pH 7, 9, and 10

	pH AFTER SATURATION WITH Na FROM SOLUTIONS AT		
	pH 7.0	pH 9.0	pH 10.0
2, paste	9.35	9.25	9.30
2, 1:10	9.90	10.05	10.05
4, paste	9.25	9.20	9.30
4, 1:10	9.90	9.90	9.90
6, paste	8.80	8.95	8.90
6, 1:10	9.40	9.55	9.50
7, paste	9.20	9.35	9.25
7, 1:10	9.85	9.90	9.85
3, paste	9.30	9.45	9.55
3, 1:10	9.80	9.90	9.90
5, paste	9.35	9.55	9.40
5, 1:10	10.10	10.15	10.10

cent methanol. The values obtained are given in table 1, showing the adsorption capacity of the soil for NH_4 when determined with neutral (pH 7.0) $N \text{ NH}_4\text{C}_2\text{H}_3\text{O}_2$, for Na from $N \text{ NaCl}$ adjusted to pH 11.1, and for NH_4 from $N \text{ NH}_4\text{C}_2\text{H}_3\text{O}_2$, adjusted to pH 8.5 following saturation of the soil with Na at pH 11.1.

The data show that the adsorbing capacity of alkaline-calcareous soils is defi-

nately increased by treatment with salt solutions of high pH values. In view of this, the next experiment was designed to determine the effect of the increased adsorption of Na on the pH value of the soil.

Twenty-gram portions of the six soils used in the previous experiment were leached with *N* sodium acetate solutions adjusted to pH 7.0, 9.0, and 10.0 until completely saturated and then were washed with successive portions of 60 per cent methanol until free from excess of salt. The pH values were determined for these soils on the soil paste and at the 1:10 soil:water ratio. These data are given in table 2. They show that despite the increased adsorption of sodium by soils leached with salt solutions of high pH values, the pH value of a soil is not increased thereby over that of the same soil when it is saturated with sodium at neutrality.

SUMMARY

The base-adsorption complex contributes to the pH of the soil by hydrolysis, and therefore the magnitude of its influence depends upon the nature of the adsorbed bases and the activity of the water in contact with the soil. Since adsorbed sodium contributes most to the high pH values in semiarid soils, the investigation was confined to this base. The results support the following conclusions:

The pH of the soil increases with increase in the percentage sodium in the complex, and the relation between the two values is significant and linear.

When the base-adsorbing complex of semiarid soils is completely saturated with sodium, all soils will have nearly the same hydrolytic pH at the 1:10 soil:water ratio regardless of the milliequivalents adsorption capacity per 100 gm. of soil. When the pH determinations are made on a soil paste, at the moisture equivalent, the pH decreases with increase in adsorbing capacity, and the correlation is highly significant and linear.

Adsorbed sodium is increased by treating the soils with solutions of sodium salts in which the pII is increased, but all the sodium-saturated soils, regardless of whether they are saturated at pH 7, 9, or 10, will have the same pH value at the 1:10 soil:water ratio.

REFERENCES

- (1) BRADFIELD, R. 1924 The importance of hydrogen-ion concentration control in physico-chemical studies on heavy soils. *Soil Sci.* 17: 411-422.
- (2) KELLEY, W. P., AND BROWN, S. M. 1924 Replaceable bases in soils. Univ. Calif. Tech. Paper 15.
- (3) McGEORGE, W. T. 1938 Factors contributing to the reaction of soils and their pH measurement. Ariz. Agr. Exp. Sta. Tech. Bul. 78.
- (4) MATTSON, S., AND HESTER, J. B. 1932 The laws of soil colloidal behavior: X. Exchange neutrality and combining capacity. *Soil Sci.* 34: 459-482.
- (5) PURI, A. N., AND UPFAL, H. L. 1939 Base exchange in soils: I. A critical examination of the methods of finding base-exchange capacity of soils. *Soil Sci.* 47: 245-253.
- (6) TIULIN, A. T., AND BYSTROVA, E. M. 1930 On the causes and mechanism of increased cation exchange in various soils after $\text{Ca}(\text{OH})_2$ treatment. *Proc. Second Internat. Cong. Soil Sci. Comn.* 2: 85-107.

SEPARATION AND IDENTIFICATION OF PHYTIN AND ITS DERIVATIVES FROM SOILS¹

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Although it is known that half or more of the total phosphorus in the surface horizons of many soils occurs in organic forms (6, 12, 14), relatively little is known of the nature and amounts of the various organic phosphorus compounds present. Nucleic acids have long been thought to make up a considerable part of soil organic phosphorus, since they are an important constituent of all plants and hence are a form of phosphorus commonly added to soil. Furthermore, all of the constituent parts of nucleic acids, including nitrogen bases, pentose sugar, and H_3PO_4 , have been obtained upon hydrolysis of soil organic phosphorus preparations (5, 16, 19, 20). The amounts of nucleic acid constituents found in the various investigations, however, are sufficient to account for only a small part of the organic phosphorus known to occur in soils, and it is evident that other types of organic phosphorus compounds must be present.

Another type of organic phosphorus compound which occurs in many plants, especially in the seeds, is phytin or inositol hexaphosphate (4, 9, 10, 11, 18). It has been shown that the partial dephosphorylation of phytin by the enzyme phytase yields phytin derivatives such as inositol triphosphate and inositol monophosphate as well as inositol and H_3PO_4 (3). There are, therefore, a number of different inositol phosphates which may conceivably occur in soils. Two recent investigations, one by Dyer *et al.* (7) and another by Yoshida (21), have dealt with the occurrence of inositol phosphates in soils. Dyer *et al.* (7) found that part of the organic phosphorus of a Quebec podzol was precipitated as a ferric salt and that the precipitate had a P:Fe ratio corresponding to that of ferric phytate similarly precipitated. The behavior of the precipitate toward dephosphorylation by various enzymes was similar to that of authentic phytin, and it was concluded that the organic phosphorus in the precipitate occurred as phytin. Yoshida (21) definitely established the presence of inositol phosphates in three Hawaiian soils. She obtained inositol and H_3PO_4 upon acid hydrolysis of soil organic phosphorus preparations and suggested on the basis of the NH_3 -N and phosphorus contents of one of her preparations that the inositol was present as the NH_4 -salt of inositol monophosphate. By the assumption of this compound, about 5 per cent of the organic phosphorus of her preparations was accounted for.

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The purpose of the present investigation was to separate and identify the various inositol phosphates present in surface soils representative of the prairie, Wiesenboden, and gray-brown podzolic great soil groups. The investigation was conducted in such a manner as to obtain approximately quantitative estimates of the amount of phosphorus present as these compounds.

EXPERIMENTAL

Soils used

The soils used were selected to represent soil organic phosphorus formed under different types of natural vegetation. Brief descriptions of the soils are given in table 1.

TABLE 1
Descriptions of soils studied

SOIL TYPE	DEPTH	GREAT SOIL GROUP	NATURAL VEGETATION	pH
	<i>inches</i>			
Carrington silt loam, cultivated.....	0-6	Prairie	Bunch grass	5.25
Webster loam, cultivated...	0-6	Wiesenboden	Marsh grass and sedges	6.20
Fayette silt loam, virgin....	0-2	Gray-brown podzolic	Hardwood trees	6.60

Extraction of soil organic phosphorus

The method used for the extraction of soil organic phosphorus was similar to that employed by Yoshida (21). Two hundred and twenty-five grams of finely ground air-dried soil was placed on a 3-inch Büchner funnel and slowly leached with 1 per cent HCl solution until the leachate no longer gave a test for Ca with NH_4 -oxalate solution. The acid-treated soil was then digested with 2,250 ml. of 2 per cent NaOH solution on a steam plate at 85–90°C. for 4 hours. Plimmer (15) has shown that phytin is highly resistant to hydrolysis under these conditions. After the soil was filtered off by means of a Büchner funnel and suction, the organic phosphorus content of the NaOH extract as well as that of the HCl extract was determined by the technique of Pearson (13), in which organic phosphorus is found by subtracting the inorganic from the total phosphorus content. All phosphorus determinations reported in this paper were made by the colorimetric method of Truog and Meyer (17), modified in that an Evelyn photoelectric colorimeter was used to measure color intensity.

Table 2 gives the amounts of organic phosphorus extracted from the soils by the HCl and the NaOH solution. The sum of the organic phosphorus extracted by these two solutions is considered to be total organic phosphorus, since second HCl and NaOH extracts of the soils contained only traces of additional organic phosphorus.³ In agreement with the results of Pearson (13) and Dyer and Wren-

³ Two per cent NaOH solution extracts slightly larger amounts of organic P from these soils than the 0.5 N NH_4OH solution used by Pearson (13).

shall (8), about 89–95 per cent of the soil organic phosphorus was removed in the alkaline extract.

Separation and identification of phytin

Since the HCl extracts of the various soils contained such small percentages of the total soil organic phosphorus, the investigation was confined to the organic phosphorus present in the NaOH extracts.

The procedure used to separate phytin was similar to that employed by Dyer *et al.* (7). Of the dark-colored NaOH extract, 2,000 ml., representing 200 gm. of soil, was oxidized by digestion with 20–25 ml. of Br₂ on a steam plate at 40–50° C. until the extract was a clear yellow color. This treatment has been shown not to decompose phytin (8). A white precipitate which formed during the oxidation of the extracts was filtered off and discarded, since analysis showed that it contained no organic phosphorus. After the clear yellow extract was acidified with 1-1 HCl and boiled to expel Br₂, its acidity was adjusted to a normality of

TABLE 2
Total amounts of organic phosphorus in soils studied

SOIL TYPE	ORGANIC P EXTRACTED BY		TOTAL ORGANIC P
	HCl	NaOH	
	<i>p.p.m.*</i>	<i>p.p.m.*</i>	<i>p.p.m.*</i>
Carrington silt loam	17	333	350
Webster loam	36	290	326
Fayette silt loam	18	298	316

* Expressed on the soil basis.

0.166 with HCl, and an excess of 5 per cent FeCl₃ solution was added. The white precipitate which formed immediately in the extract was flocculated by digestion on a steam plate for several hours. The precipitate was then separated from the liquid by means of a centrifuge and washed with small portions of 0.166 N HCl until the washings were free from inorganic phosphorus. The liquid and the washings from the precipitate were then combined and set aside to be examined for the presence of phytin derivatives.

One of the criteria used by Dyer *et al.* (7) to identify the iron precipitate obtained in their investigation was the determination of its P:Fe ratio. Though this criterion gives indicative results, it is not conclusive inasmuch as there is the possibility that iron precipitates constituents other than phytin. For positive identification, it is necessary therefore to determine the inositol:P ratios of the iron precipitates. This was accomplished in the following manner.

The iron precipitate was decomposed with 10 ml. of 2 per cent NaOH solution by heating in a water bath, the centrifuge tubes containing the precipitate. The Fe(OH)₃ which precipitated was separated from the liquid by use of a centrifuge and washed with 2–5-ml. portions of the NaOH solution. The NaOH solution used to decompose the iron precipitate and that used to wash the re-

sulting $\text{Fe}(\text{OH})_3$ were combined and adjusted to an acidity of 2 *N* with 1-1 H_2SO_4 . This solution, which contained the organic phosphorus precipitated by the iron, was then placed in a 20- by 150-mm. heavy-walled Pyrex test tube and the tube sealed by means of an oxygen burner. The contents of the tube were hydrolyzed by placing the tube overnight in an oven at 150–160° C. The tube was then opened, the contents neutralized with 10 *N* NaOH, and aliquots taken and analyzed for inorganic phosphorus and inositol. Inositol was determined by the iodomercurate method of Young (22). A determination of the inositol:P ratio of a sample of authentic ferric phytate by the above procedure agreed well with the theoretical ratio.

Table 3 gives the results of inorganic phosphorus and inositol determinations, the inositol:P ratios of the iron precipitates from the various soils, and the theoretical inositol:P ratio of phytin. The data show that the inositol:P ratios of the iron precipitates from the three soils agree closely with the theoretical

TABLE 3

Amounts of inositol and inorganic phosphorus released upon hydrolysis of the iron precipitates

SOIL TYPE	INOSITOL	INORGANIC P	INOSITOL:P RATIO FOUND*
	mgm.	mgm.	
Carrington silt loam.....	22.0	22.6	0.974
Webster loam	21.6	21.4	1.009
Fayette silt loam	15.4	15.8	0.976

* The theoretical inositol:phosphorus ratio in phytin is 0.968.

ratio of phytin and establish the fact that the organic phosphorus in the iron precipitates occurred as phytin.

Separation and identification of phytin derivatives

The combined liquid and washings obtained in the precipitations of ferric phytate in the preceding section were next examined for the presence of phytin derivatives. Anderson (1, 2) indicated that $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ precipitate all of the various phytin derivatives except inositol monophosphate. In view of the fact that the solutions to be examined for the presence of phytin derivatives possibly contained nucleic acid-like compounds, tests were made to determine whether these hydroxides would precipitate nucleic acid. It was found that this compound was precipitated to some degree by $\text{Ba}(\text{OH})_2$ but not by $\text{Ca}(\text{OH})_2$; hence it was decided to employ the latter as a precipitant for phytin derivatives other than inositol monophosphate. Since iron and inorganic phosphorus which would be precipitated by $\text{Ca}(\text{OH})_2$ were contained in the solutions to be examined, it was necessary to effect their removal. This was accomplished by precipitating the iron as $\text{Fe}(\text{OH})_3$ and the inorganic phosphorus as ammonium phosphomolybdate in dilute HNO_3 solution. The solutions were then neutralized by the addition of 10 per cent NaOH solution, and an excess of saturated $\text{Ca}(\text{OH})_2$ solution was added. The white precipitates which formed were flocculated by

heating on a steam plate, separated from the liquid by means of a centrifuge, and washed with several small portions of 2 per cent NaOH solution. The liquid and washings were set aside to be examined for the presence of inositol monophosphate. The calcium precipitates were then dissolved in 20 ml. of 2 *N* H₂SO₄, and the amounts of inositol and inorganic phosphorus released upon hydrolysis were determined by the same methods as those used in identifying the iron precipitates in the preceding section. Table 4 gives the results of the inositol and inorganic phosphorus determinations, the inositol:P ratios of the calcium precipitates from the various soils calculated from these values, and the theoretical inositol:P ratios of inositol tetraphosphate, triphosphate, and diphosphate. The inositol:P ratios of the calcium precipitates from the three soils vary more than the ratios of the iron precipitates, but all agree most closely with the theoretical ratio of inositol triphosphate. The inositol:P ratio of one

TABLE 4

Amounts of inositol and inorganic phosphorus released upon hydrolysis of the calcium precipitates

SOIL TYPE	INOSITOL	INORGANIC P	INOSITOL:P RATIO FOUND*
	<i>mgm.</i>	<i>mgm.</i>	
Carrington silt loam.....	14.8	7.6	1.95
Webster loam.....	13.0	7.0	1.86
Fayette silt loam.....	18.0	8.4	2.14

* The theoretical inositol:P ratios in inositol diphosphate, triphosphate, and tetraphosphate are, respectively, 2.90, 1.94, and 1.45.

precipitate, that from the Carrington soil, agrees almost precisely with that of the triphosphate.

As previously mentioned, Yoshida (21) obtained evidence of the presence of inositol monophosphate in one of her soil organic phosphorus preparations. Anderson (1), who first characterized this compound, asserts that it is not precipitated by iron or Ca(OH)₂; hence it would be found in the combined liquid and washings from the calcium precipitates if present. Accordingly an attempt was made to precipitate the compound from these solutions as the lead salt by the method of Anderson (1). The combined liquid and washings from the calcium precipitates were evaporated to a volume of about 250 ml., adjusted to pH 6 with acetic acid, and 5 ml. of 1 per cent lead acetate solution was added. Small amounts of white precipitates which formed in the various solutions were flocculated by heating on a steam plate and separated from the liquid by means of a centrifuge. The precipitates upon analysis were found to contain only traces of organic phosphorus and hence were discarded. A further attempt to precipitate any inositol monophosphate from the solutions with basic lead acetate was also unsuccessful. It would appear that inositol monophosphate is either absent from the NaOH extracts of the soils studied or present in quantities so small that they cannot be detected by the method employed.

The quantities of organic phosphorus remaining in the filtrates after the attempt to precipitate inositol monophosphate were found by analysis to be 13.4, 13.5, and 10.5 mgm. respectively, for the Carrington, Webster, and Fayette soils. These quantities amounted to 16.8–20.8 per cent of the total organic phosphorus originally present in the NaOH extracts of the various soils. To determine whether this organic phosphorus was a fraction resistant to oxidation by Br_2 in alkaline solution, the filtrates were made approximately 0.5 *N* with respect to NaOH by the addition of solid NaOH and digested 4 hours on the steam plate with 5 ml. of Br_2 . Determinations of the amounts of inorganic phosphorus in the filtrates after the digestion showed that between 50 and 60 per cent of the organic phosphorus had been released as inorganic phosphorus. Hence it is apparent that the organic phosphorus remaining in the filtrates after the removal of inositol phosphates is not a fraction stable toward alkaline bromination, but consists of organic phosphorus compounds of a type other than phytin which was not decomposed during the first treatment with alkaline Br_2 .

TABLE 5

Amounts of phosphorus present as phytin and phytin derivatives in the NaOH extracts of soils

SOIL TYPE	(A)	(B)		(C)		TOTAL P PRESENT AS PHYTIN AND ITS DERIVATIVES SUM OF (B) AND (C)	
	TOTAL ORGANIC P	P PRESENT AS PHYTIN		P PRESENT AS PHYTIN DERIVATIVES		p.p.m.*	per cent of (A)
	p.p.m.*	p.p.m.*	per cent of (A)	p.p.m.*	per cent of (A)		
Carrington silt loam.....	333	113	34.0	38	11.4	151	45.4
Webster loam.....	290	107	36.9	35	12.1	142	49.0
Fayette silt loam.....	298	79	26.5	42	14.1	121	40.6

* Expressed on the soil basis.

Amounts of organic phosphorus present as phytin and phytin derivatives

The amounts of organic phosphorus present as phytin and its derivatives in the NaOH extracts of the various soils as well as the percentages of the total organic phosphorus in the extracts present as these compounds are given in table 5. It will be noted that the percentages of the total organic phosphorus which were present as phytin in the NaOH extracts varied from 26.5 in the Fayette soil to approximately 35 in the Carrington and Webster soils. The percentages of the total organic phosphorus present as phytin derivatives are similar in the three soils and considerably less than the phytin-phosphorus percentages. Of the total organic phosphorus of the NaOH extracts of the soils, 40 to 49 per cent occurred as phytin and its derivatives. The percentages of the total soil organic phosphorus present as phytin and its derivatives undoubtedly approximates these values, since the NaOH extracts contained 89–95 per cent of the total soil organic phosphorus.

DISCUSSION

The results of this investigation establish the presence of phytin and phytin derivatives in soils representative of the prairie, Wiesenboden, and gray-brown

podzolic great soil groups. Moreover, these compounds were isolated in a manner which is believed to give approximately quantitative estimates of the amounts present. Nearly half of the total organic phosphorus of the various soils was present as phytin and its derivatives. Of this amount approximately three fourths occurred as phytin. The fraction of soil organic phosphorus identified as phytin derivatives had an inositol:P ratio corresponding most closely with that of inositol triphosphate but was probably a mixture of inositol diphosphate, triphosphate, and tetraphosphate with the triphosphate predominating. No inositol monophosphate was detected in the NaOH extracts of any of the soils studied.

The large amounts of phytin and phytin derivatives found in the soils studied and the evidence obtained by Dyer *et al.* (7) and Yoshida (21) of the presence of inositol phosphates in podzol and lateritic soils, respectively, make it increasingly evident that these organic phosphorus compounds are of general occurrence in soils.

Apparently several if not all of the various inositol phosphates may occur in one soil or another. Wrenshall and Dyer (20) obtained evidence only of the presence of phytin but recognized the possibility of the occurrence of other inositol phosphates formed by the partial dephosphorylation of phytin. These investigators suggested, however, that phytin would tend to persist as such in soils since it forms insoluble ferric and aluminum salts that are stable toward decomposition by the phytase enzyme. On the other hand, some of Yoshida's data (21) indicate that the inositol phosphate found in her preparations was inositol monophosphate. She argued that the phytin in plant materials added to soils probably is converted to phytin derivatives before sufficient ferric and aluminum is available to fix the phytin as suggested by Dyer and Wrenshall. The present investigation establishes the fact that considerable quantities both of phytin and of phytin derivatives may occur in the same soil. The isolation of phytin derivatives from the soils studied is evidence that the decomposition of phytin takes place in soils. The data indicate that the decomposition is not very rapid, however, since the amounts of phytin-phosphorus found were much larger than the amounts of phosphorus occurring as phytin derivatives.

SUMMARY

In a study of soil organic phosphorus, surface soils representative of the prairie (Carrington silt loam), Wiesenboden (Webster loam), and gray-brown podzolic (Fayette silt loam) great soil groups were investigated to determine their contents of phytin and phytin derivatives. Phytin was precipitated as the ferric salt and phytin derivatives as their calcium salts from NaOH extracts, which contained 89-95 per cent of the total soil organic phosphorus. The iron and calcium precipitates from the various soils were identified by comparing their inositol:P ratios with the theoretical ratios of phytin and its various derivatives.

Approximately 35 per cent of the total organic phosphorus in the NaOH extracts of the Carrington and Webster soils and 26.5 per cent of that in the extracts of the Fayette soil occurred as phytin. The phytin derivatives precipitated by calcium from the NaOH extracts of the various soils had an inositol:P

ratio corresponding most closely with that of inositol triphosphate but were probably a mixture of the diphosphate, triphosphate, and tetrphosphate forms, with the triphosphate predominating. The amounts of phytin derivatives isolated from the various soils ranged from 11.4 to 14.1 per cent of the total organic phosphorus of the NaOH extracts. An attempt to isolate inositol monophosphate from the various soils by precipitation as the lead salt was unsuccessful.

The isolation of considerable amounts of phytin and phytin derivatives from the soils studied indicates that these organic phosphorus compounds constitute an important form of soil organic phosphorus. Furthermore, the isolation of phytin derivatives as well as phytin is evidence of the decomposition of phytin in soils. The decomposition is not very rapid, however, since the amounts of phytin-phosphorus found were much larger than the amounts of phosphorus occurring as phytin derivatives.

REFERENCES

- (1) ANDERSON, R. J. 1914 Concerning the organic phosphoric acid compound of wheat bran: III. Inosite monophosphate, a new organic phosphoric acid occurring in wheat bran. *Jour. Biol. Chem.* 18: 441-446.
- (2) ANDERSON, R. J. 1915 Concerning the organic phosphoric acid compound of wheat bran: IV. The occurrence of inosite triphosphate in wheat bran. *Jour. Biol. Chem.* 20: 463-473.
- (3) ANDERSON, R. J. 1915 The hydrolysis of phytin by the enzyme phytase contained in wheat bran. *Jour. Biol. Chem.* 20: 475-482.
- (4) AVERILL, H. P., AND KING, C. G. 1926 The phytin content of foodstuffs. *Jour. Amer. Chem. Soc.* 48: 724-728.
- (5) BOTTOMLEY, W. B. 1919 The isolation from peat of certain nucleic acid derivatives. *Proc. Roy. Soc. [London] (B)* 90:39-44.
- (6) DICKMAN, S. R., AND DE TURK, E. E. 1938 A method for the determination of the organic phosphorus of soils. *Soil Sci.* 45: 29-39.
- (7) DYER, W. J., WRENSHALL, C. L., AND SMITH, G. R. 1940 The isolation of phytin from soil. *Science* 91: 319-320.
- (8) DYER, W. J., AND WRENSHALL, C. L. 1941 Organic phosphorus in soils: I. The extraction and separation of organic phosphorus compounds from soil. *Soil Sci.* 51: 159-170.
- (9) HENRICI, M. 1927 Phosphormangel als Ursache von Störungen Leben der Pflanze. *Verhandl. Naturf. Gesell. Basel.* 38: 316-326.
- (10) KNOWLES, F., AND WATKINS, J. E. 1932 The amount and distribution of some phosphorus and nitrogen compounds in wheat during growth. *Jour. Agr. Sci.* 22: 755-766.
- (11) McCANCE, R. A., AND WIDDOWSON, E. M. 1935 Phytin in human nutrition. *Biochem. Jour.* 29: 2694-2699.
- (12) ODYNSKY, W. 1936 Solubility and distribution of phosphorus in Alberta soils. *Sci. Agr.* 16: 652-664.
- (13) PEARSON, R. W. 1940 Determination of organic phosphorus in soils. *Indus. and Engin. Chem., Analyt. Ed.* 12: 198-200.
- (14) PEARSON, R. W., AND SIMONSON, R. W. 1940 Organic phosphorus in seven Iowa soil profiles: distribution and amounts as compared to organic carbon and nitrogen. *Soil Sci. Soc. Amer. Proc.* 4: 162-167.
- (15) PLIMMER, R. H. A. 1913 The hydrolysis of organic phosphorus compounds by dilute acid and by dilute alkali. *Biochem. Jour.* 7: 72-80.

- (16) SHOREY, E. C. 1913 Some organic soil constituents. U. S. Dept. Agr. Bur. Soils Bul. 88.
- (17) TRUOG, E., AND MEYER, A. H. 1929 Improvements in the Denigès colorimetric method for phosphorus and arsenic. *Indus. and Engin. Chem., Analyt. Ed.* 1: 136-139.
- (18) WEBSTER, J. E. 1928 Phosphorus distribution in grains. *Jour. Agr. Res.* 37: 123-125.
- (19) WRENSHALL, C. L., AND MCKIBBIN, R. R. 1937 Pasture studies: XII. The nature of the organic phosphorus in soils. *Canad. Jour. Res. (B)* 15: 475-479.
- (20) WRENSHALL, C. L. AND DYER, W. J. 1941 Organic phosphorus in soils: II. The nature of the organic phosphorus compounds. A. Nucleic acid derivatives. B. Phytin. *Soil Sci.* 51: 235-248.
- (21) YOSHIDA, R. K. 1940 Studies on organic phosphorus compounds in soil; isolation of inositol. *Soil Sci.* 50: 81-89.
- (22) YOUNG, L. 1934 The volumetric determination of inositol. *Biochem. Jour.* 28: 1435-1443.

INFLUENCE OF MICROORGANISMS AND SOME ORGANIC SUBSTANCES ON SOIL STRUCTURE¹

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Organic matter has been shown to influence the physical properties of the soil (3, 4, 8, 9-14). The decomposition products of soil microorganisms increased considerably the water intake of straw-mulched Peorian loess (6).

Little information is available on the constituents of the soil organic matter that increase soil-structure stability to water. Alderfer, Gribbins, and Haley (1) showed that the lignin in waste sulfite liquor had a marked effect on soil aggregation.

The purpose of this investigation was to determine the influence of microorganisms and some specific substance or group of substances that might occur in organic matter on soil-structure stability to water drops.

EXPERIMENTAL METHOD

Soil-structure stability was determined by the water-drop method (7), in which a soil lump of approximately 0.15 gm. (air-dry weight) was placed on a 1-mm. mesh screen and water drops of 4.7 mm. diameter, falling from a height of 30 cm. at a rate of 1 drop per 1.5 seconds, were allowed to strike it. The structure was considered destroyed when the aggregate had been broken down and was at the point of being washed through the screen. The results were expressed as drops per 0.1 gm. of soil and represent the mean of two sets of 20 determinations each, making a total of 40 tests for each result reported.

SOIL STUDIED

In order to determine the influence of microbiological and organic agents on soil structure, it was thought desirable to work with a material very low in organic matter. Accordingly, a supply of the parent material of Peorian loess was obtained from about 10 feet below the surface in a road cut near Plattsmouth, Nebraska. This contained 0.25 per cent readily oxidizable material. The Peorian loess was broken up, and small lumps of about 0.15 gm., as shown in figure 1, were separated by screening. The various treatments were applied to these air-dried lumps. Water was not added in amounts to exceed the optimum moisture content, and therefore the natural structure was not destroyed by puddling.

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INFLUENCE OF VARIOUS BIOLOGICAL, PHYSICAL, AND CHEMICAL FACTORS
ON STABILITY

Soil types

For comparative purposes the number of water drops required to break down the structure of eight different air-dried topsoils and two samples of Peorian loess are shown in table 1. The eight topsoils containing animate and inanimate organic substances required two to six times as much water to destroy the structure as did the untreated Peorian loess, which was almost devoid of organic substances.

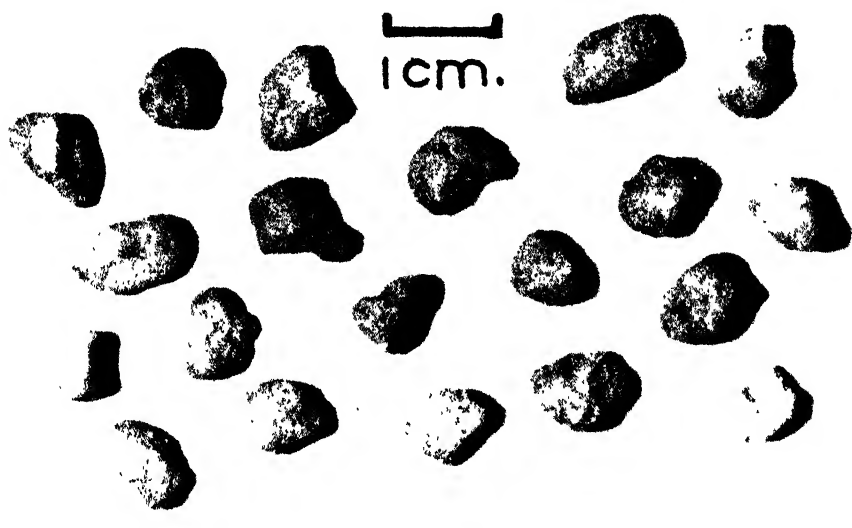


FIG. 1. SIZE AND SHAPE OF LUMPS OF PEORIAN LOESS TO WHICH VARIOUS TREATMENTS WERE APPLIED

Each lump weighed approximately 0.15 gm

A

B

C

Browning, Russell, and McHenry (3) found that the number of water drops required to destroy the soil structure of 13 different Iowa soils varied from 13 to 325.

Microbial activity

Dry, ground wheat straw, mature sweetclover, and dextrose were added to lumps of Marshall topsoil and Peorian loess in petri dishes at the rate of 2, 4, 8, and 16 tons per acre. The lumps were brought up to approximately optimum moisture content with water containing 1 gm. of ammonium nitrate per liter and a small amount of inoculation from a topsoil, and maintained there during a period of incubation at 28° C. Periodically twenty lumps were taken from each treatment and air-dried. The stability to water drops was determined. The entire experiment was repeated later, and the results represent the mean of the two tests, or 40 determinations, as shown in tables 2 and 3.

In every instance where energy material was added which would stimulate microbiological activity, the stability of the soil structure to water drops was increased. The dextrose, wheat straw, or sweetclover prior to microbial activity

TABLE 1

Number of water drops required to break down the structure of several Nebraska soils

SOIL TYPE	DESCRIPTION	DROPS PER 0.1 GM. SOIL
Knox silt loam	Virgin	29.5
Knox silt loam	Parent material (10 to 15 feet)	4.3
Marshall silty clay loam	Topsoil cultivated	9.8
Hastings silt loam	Topsoil	12.3
Hastings silt loam	Subsoil (6 feet)	5.1
Wabash silt loam*	Topsoil	11.1
Marshall silt loam*	Topsoil	12.8
Carrington silt loam*	Topsoil	13.1
Moody silt loam*	Topsoil	18.3
Laurel fine sandy loam*	Topsoil	21.1

* These samples were obtained through the kindness of J. W. Fitts, agronomy department, University of Nebraska

TABLE 2

Effect of transformation of noneffective substances into microbial tissue or by-products on the structure stability of Peorian loess

SUBSTANCE ADDED TO PEORIAN LOESS	RATE OF APPLICATION PER ACRE	DAYS OF INCUBATION						
		0	4	6	10	16	30	60
	<i>tons</i>	<i>Drops per 0.1 gm. soil</i>						
None		4.5	4.0	4.3	5.1	5.3	5.2	
Dextrose	2	4.5	5.8	5.7	6.4	5.4	5.7	5.9
	4	4.5	11.0	10.1	20.3	6.0	6.2	5.6
	8	4.5	14.3	86.1	92.2	27.6	9.3	6.6
	16	4.5	19.1	351.1	136.7	38.2	28.8	8.8
Wheat straw	2	4.5	5.7	5.3	6.4	5.4	5.2	5.4
	4	4.5	5.7	6.5	8.2	6.8	5.6	7.5
	8	4.5	6.1	6.8	9.4	6.5	6.6	7.9
	16	4.5	6.4	10.1	14.6	8.3	7.5	8.2
Sweetclover	2	4.5	4.4	5.0	6.5	5.5	5.5	5.6
	4	4.5	5.1	5.7	7.7	7.0	6.9	7.6
	8	4.5	5.9	6.6	10.0	8.1	7.1	7.9
	16	4.5	5.0	7.5	10.7	9.7	7.5	8.4

had no effect on the stability of the soil structure to water drops. The 4-ton rate of application of dextrose to the Peorian loess increased the structure stability beyond that of the cultivated Marshall topsoil, which is 9.8 drops per 0.1 gm. of

soil. The 8- and 16-ton rates of application to the Peorian loess increased the stability tremendously. This was probably due largely to a mass of mycelia which bound the lumps into a compact unit not easily broken down by the water drops. This highly water-stable condition did not last long and did not occur to the same degree with the sweetclover or wheat-straw residues. The applications of wheat straw and sweetclover at the rates of 2 and 4 tons per acre to the Peorian loess produced a stability less than that of the Marshall topsoil (table 1). The applications at the rates of 8 and 16 tons per acre to the Peorian loess produced a stability equal to that of the Marshall topsoil but considerably less than that of the virgin Knox topsoil.

TABLE 3

Effect of transformation of nonreflective substances into microbial tissue or by products on the structure stability of Marshall topsoil

SUBSTANCE ADDED TO MARSHALL TOPSOIL	RATE OF APPLICATION PER ACRE	DAYS OF INCUBATION					
		0	3	8	18	30	60
		<i>Drops per 0.1 gm. soil</i>					
None	<i>tons</i>	9.7	9.4	9.6	10.1	9.7	
Dextrose	2	9.7	24.1	11.4	13.6	10.5	9.6
	4	9.7	29.5	22.4	24.4	14.1	10.3
	8	9.7	45.3	105.2	44.2	18.3	10.7
	16	9.7	58.7	243.5	43.1	27.6	11.3
Wheat straw	2	9.7	10.9	12.4	10.1	9.1	10.7
	4	9.7	12.1	11.2	12.3	9.4	11.2
	8	9.7	14.3	17.2	14.1	13.0	10.1
	16	9.7	14.2	20.8	22.3	17.3	9.9
Sweetclover	2	9.7	10.2	9.1	9.2	9.8	8.9
	4	9.7	11.7	13.4	13.8	11.4	8.8
	8	9.7	11.6	14.9	12.6	13.8	9.2
	16	9.7	12.1	15.7	16.0	15.3	9.6

In every instance, the stability of the Marshall topsoil to water drops was increased, by the addition of energy material, beyond that found in the normal cultivated condition. The period of increased stability was short, however, and was followed by a rapid decline and to the original stability.

When plant residues were returned to the soil there was an increased stability concomitant with the microbial activity. The biological type of stability is necessarily temporary, depending on the length and degree of microbial activity. A state of microbial activity may be maintained by the continued addition of energy material to the soil.

Moisture content

Wheat straw at the rate of 8 tons per acre was added to petri dishes containing lumps of Peorian loess weighing approximately 0.15 gm. The treated and the

untreated Peorian loess were kept at approximately optimum moisture content and a temperature of 28° C. At different intervals of time 10 lumps were taken from each treatment. Twenty of the lumps were tested immediately in a moist condition (about 25 per cent water), and twenty were air-dried and then tested for stability to water drops. Neither the dry nor the moist condition of the untreated Peorian loess lumps affected the stability to water drops. The lumps receiving finely ground wheat straw at the rate of 8 tons per acre, however, were more stable in the moist condition. The microbial decomposition products were more stable in the moist condition, as shown in table 4. This may be due to the greater stability to water drops of the decomposition products in the initial wet condition. When the soil lumps are dried and rewet they do not return to the

TABLE 4
Influence of decaying organic matter and moisture content on stability of Peorian loess to water drops

TREATMENT	SOIL CONDITION	DAYS OF INCUBATION			
		0	7	14	30
<i>Drops per 0.1 gm. soil</i>					
None	Moist	4.3	4.4	5.0	4.2
	Dry	4.4	4.3	4.0	4.5
Straw, 8 tons per acre	Moist	4.3	15.1	14.2	11.0
	Dry	4.4	7.8	8.1	7.6

original high degree of stability. These decomposition products, once dehydrated or partly dehydrated, lose a part of their stabilizing effect on soil structure, probably because the microbial filaments, on drying, break into pieces.

Extracted substances from wheat straw

Alcohol-benzene, hot water, and 1 per cent HCl extracts were made from wheat straw by the method of the A. O. A. C. (2). Lignin was extracted, with 10 per cent NaOH in the autoclave at 15 pounds' pressure for 2 hours, from the straw that had been treated with alcohol-benzene, hot water, and 1 per cent HCl. The materials left after this treatment were designated as the cellulose. The lignin was precipitated with HCl and then washed free of electrolytes with distilled water by centrifuging and decanting. The cellulose suspension was also washed free of excess electrolytes with distilled water. Determinations were made of the amount of material in solution or suspension by drying an aliquot in the oven at 105° C. The suspension or solution of material was then added to lumps of the Peorian loess to make concentrations of 0.25, 0.50, 1.00, 2.00, and 4.00 per cent, dried in the oven immediately at 105° C., and the structure stability determined, as shown in table 5.

The group of compounds including the waxes and fatty substances increased the stability of the soil, as did also the lignins, but the other groups of compounds—carbohydrates, celluloses, and hemicelluloses—had no measurable effect.

An excess of the various fat solvents was added to Peorian loess and Marshall topsoil lumps and allowed to evaporate. The samples were then tested for stability. The data are shown in table 6.

None of the fat solvents seemed to extract a substance from the Peorian loess that would change the stability of the soil structure to water drops. The stability of the topsoil, however, was reduced by the solvents. Since soil organic matter is composed of about 1 to 3 per cent alcohol-ether-soluble material (12),

TABLE 5

Influence of different extracts of wheat straw on stability of Peorian loess to water drops

SUBSTANCES EXTRACTED	REAGENT FOR EXTRACTING WHEAT STRAW*	CONCENTRATION				
		0.25%	0.50%	1.00%	2.00%	4.00%
		<i>Drops per 0.1 gm. soil</i>				
Waxes, fats, etc	Alcohol benzene	4.6	4.7	13.4	53.5	87.1
Carbohydrates, etc	Hot water	4.3	1.5	4.3	4.2	4.5
Hemicelluloses, etc	1 per cent HCl	4.0	4.4	4.2	1.5	4.6
Lignins, etc	10 per cent NaOH	6.7	9.1	17.0	24.7	36.0
Celluloses, etc	Left after NaOH extraction	4.2	4.2	4.6	4.3	4.2

* With no reagent (check), the stability was 1.5 drops per 0.1 gm. soil.

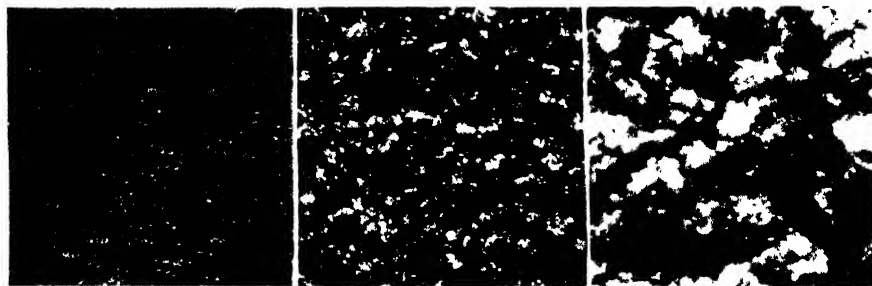


FIG. 2. AGGREGATES RESULTING FROM THE TREATMENT OF PEORIAN LOESS WITH VARIOUS AGENTS, $\times 14$

A, Treated with benzene and slaked in water; B, treated with water and slaked in water; C, treated with glacial acetic acid and slaked in water

this fraction would not be expected to influence soil stability as much as some of the other soil organic matter fractions. The treatment of the Peorian loess with benzene did decrease the size of aggregates (fig. 2). This seems to indicate that the aggregates were held together to a certain degree, by a substance extracted by benzene.

Inorganic salts, acids, and organic dyes

Since plants or plant materials, upon decay, will supply some salts or acids which would be present in the humus fraction or in the soil, the effect of some of these substances on soil structure stability to water drops was determined.

The inorganic salts and acids were dissolved in distilled water. The acid and basic dyes were dissolved in 95 per cent ethyl alcohol. These were added to

TABLE 6
Influence of fat solvents on soil structure stability to water drops

FAT SOLVENT	PEORIAN LOESS	MARSHALL TOPSOIL
	<i>Drops per 0.1 gm. soil</i>	
None.....	4.2	19.4
Alcohol-benzene.....	4.2	14.8
Ether.....	4.2	14.4
Acetone.....	4.4	15.6

TABLE 7
Influence of some inorganic salts, acids, and dyes on the stability of Peorian loess to water drops

SUBSTANCE ADDED TO PEORIAN LOESS*		CONCENTRATION		
		0.25%	0.50%	1.00%
		<i>Drops per 0.1 gm. soil</i>		
Inorganic salts	NaCl.....	4.2	4.3	4.1
	KNO ₃	4.3	4.1	4.2
	CaCO ₃	4.0	4.2	4.1
	MgSO ₄	4.2	4.3	4.2
	FeCl ₃	4.3	4.2	4.4
Acids	HCl.....	4.5	4.5	4.7
	Acetic.....	4.4	4.6	4.3
	Oxalic.....	4.3	4.3	4.2
	Citric.....	4.1	4.6	4.0
	Boric.....	4.6	4.4	4.4
	Picric.....	4.5	4.5	4.5
	Tannic.....	4.2	4.3	4.3
	Stearic.....	5.5	8.9	7.8
Acid dyes	Congo red.....	4.7	4.8	4.8
	Alizarine red.....	4.8	4.9	5.1
	Eosin.....	5.1	5.3	5.6
	Rose bengal.....	5.7	5.8	6.4
Basic dyes	Neutral red.....	5.1	5.6	5.9
	Fuchsin.....	5.8	6.4	7.2
	Methylene blue.....	5.8	6.0	5.9
	Brilliant green.....	7.6	10.0	18.2

* When no substance was added (check), the stability was 4.4 drops per 0.1 gm. soil.

lumps of Peorian loess in 0.25, 0.50, and 1.00 per cent concentration, respectively. Samples were dried at 105° C. and tested immediately (table 7).

Sodium, potassium, calcium, magnesium, and iron with their respective anions of chloride, nitrate, carbonate, sulfate, and chloride did not affect the stability of

the soil structure to water drops, even in 1 per cent concentration. It is unlikely, therefore, that the inorganic nutrients liberated during the decay of crop residues or humus would affect the stability of the Peorian loess to water drops.

In concentrations of 0.25, 0.50, and 1 per cent, none of the acids tested, except stearic, had any influence on the stability of the soil structure to water drops. When large chunks of Peorian loess were treated with glacial acetic acid and slaked in distilled water, aggregation increased. When the same soil was treated with benzene, the aggregation units were decreased in size, as shown in figure 2. Treatment of Peorian loess with concentrated HCl or H₂SO₄ produced a granular structure highly stable to water drops.

Organic acids may be produced in low concentration in the soil during decomposition of organic matter, or probably by the plant roots during growth. It seems that, because of low concentration, however, they may not be of much significance in producing soil-structure stability to water drops.

Except for the slight effect of rose bengal and eosin, the acid dyes had no effect on stability. Some of the basic dyes more than doubled the stability to water drops. Thus some of the strongly adsorbed organic substances appear to influence the stability to water drops.

Wetting agents

A number of commercial wetting agents were dissolved in distilled water and added to lumps of Peorian loess and Marshall topsoil to make concentrations of 0.25, 0.50, and 1.00 per cent. The treated soils were then dried in an oven at 105° C. (table 8).

It has been shown (7) that wetting of the Peorian loess was largely responsible for the loss of stability. About 1,000 gm. of force was required to break a dry lump of Marshall topsoil or Peorian loess, whereas only 0.5 gm. of water was required to destroy the Peorian loess, and 1 to 3 gm., the Marshall topsoil. Wetting would then appear as an important factor in soil destruction by water drops, and any substance increasing wetting should increase structure deterioration, but the Peorian loess seemed to wet rapidly even before treatment by wetting agents.

The wetting agents, with the exception of Dresinate, which had a slightly stabilizing effect, had very little effect on the stability of Peorian loess to water drops. They reduced the stability of the Marshall topsoil.

Carbohydrates, proteins, gums, oils, fats, waxes, rosin, and paraffin

Carbohydrates, proteins, and gums were dissolved in distilled water and added to lumps of Peorian loess, and waxes, oils, fats, rosin, and paraffin were dissolved in an alcohol-benzene mixture and added. After the alcohol-benzene mixture had evaporated, all samples were dried immediately at 105° C. and determinations made, as shown in table 9.

None of the carbohydrates and few of the proteins were effective in increasing the structure stability of Peorian loess to water drops. Egg albumin and casein, however, were highly effective. The lumps seemed to wet rather quickly but did

TABLE 8

Influence of wetting agents on stability of Peorian loess and Marshall top soil to water drops

SUBSTANCE ADDED*		CONCENTRATION		
		0.25%	0.50%	1.00%
<i>Peorian loess</i>				
		<i>Drops per 0.1 gm. soil</i>		
Wetting agents	Nuconol.....	4.9	4.9	5.0
	Intramine.....	4.7	4.9	4.7
	Ultrawet.....	4.9	5.1	5.1
	Wetanol.....	4.5	4.8	5.0
	Cominol.....	4.8	5.3	5.0
	Drescinate.....	5.6	7.4	7.4
<i>Marshall topsoil</i>				
Wetting agents	Wetanol.....	15.4	9.1	10.3
	Ultrawet.....	14.3	11.1	11.2

* When no substance was added, the stability of Peorian loess was 4.8 drops per 0.1 gm soil, and that of Marshall topsoil, 16.6 drops.

TABLE 9

Influence of carbohydrates, proteins, oils, waxes, and gums on the stability of Peorian loess to water drops

SUBSTANCE ADDED*		CONCENTRATION		
		0.25%	0.50%	1.00%
		<i>Drops per 0.1 gm. soil</i>		
Carbohydrates	Dextrose.....	4.3	4.5	4.4
	Sucrose.....	4.0	4.2	4.3
	Dextrin.....	4.3	4.1	4.2
	Salicin.....	4.7	4.8	4.6
	Starch.....	4.2	4.5	4.4
Proteins	Urea.....	4.4	4.0	4.2
	Tryptone.....	4.3	4.1	4.3
	Asparagine.....	4.2	4.1	4.3
	Peptone.....	4.2	4.2	4.2
	Egg Albumin.....	270.0	1060.0	4000.0
	Casein.....	31.4	224.0	1369.0
Gums	Arabic.....	4.2	4.2	4.3
Oils	Vegetable	14.4	13.4	14.9
Fats	Vegetable	13.5	13.9	15.4
Waxes	Ceresin.....	5.7	12.5	30.4
	Beeswax.....	6.5	9.4	11.9
Rosin		11.6	16.3	17.6
Paraffin		12.7	20.2	23.9

* When no substance was added to Peorian loess, the stability was 4.4 drops per 0.1 gm. soil.

not swell and disintegrate from the pounding of the water drops except after a long time. The oils, fats, waxes, rosin, and paraffin in the concentrations used increased the stability of the soil structure to water drops. These lumps wet slowly and did not appear to swell.

DISCUSSION

After a few days of incubation, microorganisms were able to transform wheat or sweetclover residues present in 0.8 per cent concentration into substances which stabilized Peorian loess to a degree equal to that of the Marshall topsoil, which contained approximately 4 per cent organic matter. Maintenance of stability, therefore, does not seem to be entirely a problem of quantity of organic matter present; the quality or state of decomposition of the organic matter appears to be more important. The mere presence of organic matter in the form of particles, such as finely divided cellulose, or in a soluble form, as certain carbohydrates on or in the loess subsoil, does not increase the stability to water drops. These substances must be in a biologically decomposing state in order to influence stability. Such a source of soil-structure stability is necessarily temporary, and for its maintenance, biological activity must be continued. This can be accomplished by successive additions of plant material to the soil. Thus a "turnover" in biological activity in the soil can be brought about by returning plant residues to the soil periodically. The residues in the process of decomposition produce an interval of increased stability to the soil structure. Plant nutrients are released from the organic matter during decay to produce another growth of plants, which in turn can be returned to the soil³ to repeat the biological activity, resulting in increased structure stability to water drops for a period of time.

Of the organic compounds tested for their influence on the stability of soil structure to water drops, the lignins, oils, fats, waxes, rosin, paraffin, and colloidal proteins seemed to be the most effective. Since about three fourths of the soil organic matter is composed of lignin and proteins (12), these substances are probably largely responsible for the stabilizing effect of organic matter. The microorganisms themselves, particularly fungi, in sufficient number and distribution seem to bind the soil together. Many of the water-soluble organic substances were without effect on soil structure. The soil microorganisms, however, could almost immediately transform the noneffective compounds into substances or microbial tissue that would be effective in temporarily stabilizing the soil structure.

SUMMARY

Knox topsoil, with an accumulation of decomposition products, was found to have a much higher stability to water drops than Peorian loess devoid of these

³ Many grasses annually produce 2 to 4 tons of dry plant material per acre above the soil, and approximately the same amount of roots may be found in a mature crop. In addition, there is the growth of many other soil organisms that get their carbon from carbon dioxide. During the growth of the plants, organic substances are liberated to the soil organism which result in a tenfold increase in microbial activity in the vicinity of the root (5).

products. When wheat straw, sweetclover, or dextrose was added and allowed to decay in Peorian loess, the stability to water drops was increased temporarily. The amount of water required for structure destruction was increased from slightly in some cases to many fold in others over the untreated soil.

Many organic substances, dextrose, sucrose, starch, peptone, cellulose, and gum arabic, did not contribute to soil-structure stability, though these substances do furnish energy material for soil microorganisms, which can convert them readily into either microbial tissue or decomposition products that increase soil-structure stability. Lignin, proteins, oils, fats, waxes, rosin, and paraffin increased the stability of lumps of Peorian loess to water drops. Inorganic salts did not increase the stability. Of several wetting agents added to Peorian loess, one increased stability, whereas the others had no effect. They decreased the stability of Marshall topsoil. Some of the strongly adsorbed organic substances such as the basic dyes increased slightly the stability of the Peorian loess.

Increased structure stability resulting from biological activity is temporary, apparently remaining as long as the stabilizing decomposition products exist.

Quantity of organic matter does not seem so important as quality in producing stability to water drops. It would appear from these results that any substance decreasing the rate of wetting or the swelling of the soil would increase its structure stability to water drops.

REFERENCES

- (1) ALDERFER, R. B., GRIBBINS, M. F., AND HALEY, D. E. 1944 Effect of waste sulfite liquor on aggregation of soil particles. *Indus. and Engin. Chem.* 36: 272-274.
- (2) ANONYMOUS 1940 Methods of Analysis of the Association of Official Agricultural Chemists, ed. 5. George Banta Publishing Co., Menasha, Wis.
- (3) BROWNING, G. M., RUSSELL, M. B., AND MCHENRY, J. R. 1943 A comparison of methods for determining and expressing soil aggregation data. *Soil Sci. Soc. Amer. Proc.* 8: 91-96.
- (4) BROWNING, G. M., AND MILAM, F. M. 1944 The effect of different types of organic materials and lime on soil aggregation. *Soil Sci.* 57: 91-106.
- (5) CLARK, F. E. 1940 Notes on types of bacteria associated with plant roots. *Trans. Kansas Acad. Sci.* 43: 75-84.
- (6) MCCALLA, T. M. 1942 Influence of biological products on soil structure and infiltration. *Soil Sci. Soc. Amer. Proc.* 7: 209-214.
- (7) MCCALLA, T. M. 1944 Water-drop method of determining stability of soil structure. *Soil Sci.* 58: 117-123.
- (8) MCHENRY, J. R., AND RUSSELL, M. B. 1944 Microbial activity and aggregation of mixtures of bentonite and sand. *Soil Sci.* 57: 351-357.
- (9) MYERS, H. E. 1937 Physiochemical reactions between organic and inorganic soil colloids as related to aggregate formation. *Soil Sci.* 44: 331-359.
- (10) MYERS, H. E., AND MCCALLA, T. M. 1941 Changes in soil aggregation in relation to bacterial numbers, hydrogen-ion concentration and length of time soil was kept moist. *Soil Sci.* 51: 189-200.
- (11) SHRIKHANDE, J. G. 1933 The production of mucus during the decomposition of plant material. *Jour. Biochem.* 27: 1551-1574.
- (12) WAKSMAN, S. A. 1938 Humus. The Williams & Wilkins Company, Baltimore, Md.
- (13) WELDON, T. A., AND HIDE, J. C. 1942 Some chemical properties of soil organic matter and of sesquioxides associated with aggregation in soils. *Soil Sci.* 54: 343-352.
- (14) WILLIAMS, W. R. 1935 Thesis of tenacity and cohesion in soil structure. *Pedology*, nos. 5 and 6: 755-762.

EFFECTS OF SEVERAL NITROGENOUS FERTILIZERS AND SOIL AMENDMENTS ON THE PHYSICAL AND CHEMICAL PROPERTIES OF AN IRRIGATED SOIL¹

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Not the least among the many advantages of long-term fertilizer experiments are the opportunities provided for determining, under a given complex of soil, climate, cropping, and cultural practices, the ultimate effects of differential fertilization on soil properties and, in turn, the influence of these on soil productivity. Many long-term fertilizer trials are in progress on various soils of the humid regions, but very few such experiments exist on the irrigated soils of the semiarid regions. One of the oldest and most extensive of the latter is the citrus fertilizer experiment at the University of California Citrus Experiment Station, Riverside, California (1, 7). This experiment consists of 44 different fertilizer treatments and involves an area of nearly 50 acres.

The orchard was planted in 1917, and from this date to 1927 no fertilizer was applied to any of the trees. During this period, winter cover crops of yellow bitter clover (*Melilotus indica*) or purple vetch (*Vicia atropurpurea*) were grown annually throughout the orchard; and for the first 6 years of the period, summer cover crops of black-eye beans or cowpeas (*Vigna sinensis*) were also grown.

In the spring of 1927, differential fertilization was begun. In those treatments which are the subject of the present study, various nitrogenous fertilizers, including ammonium sulfate and sodium nitrate, were applied at the rate of 1 pound of nitrogen per tree annually through 1939. During this 12-year period, tree response to these treatments was almost identical (7). In the spring of 1940, with the appearance of symptoms of incipient nitrogen deficiency throughout the plots, the rate of nitrogen application was increased to 3 pounds per tree annually. In contrast to the earlier uniform response, marked changes in tree condition began to appear in certain plots in the summer and fall of 1942.

A careful survey of the fertilizer treatments at this time revealed that the trees in all the plots receiving either ammonium sulfate or sodium nitrate were in extremely poor condition; they were badly defoliated, the crops were exceedingly small, and many branches were dying back from the tip. In contrast, the trees in plots receiving equivalent amounts of nitrogen from calcium nitrate or from manure were in good condition. The condition of the trees in the urea plots was good, though perhaps not quite so good as that of the trees in the calcium nitrate and manure plots. The trees in the plots receiving sodium nitrate and gypsum showed almost no signs of distress, nor did those in the plots

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receiving ammonium sulfate and limestone. A more complete account of the influence of the various fertilizers on tree condition has been given by Parker, Chapman, and Aldrich.³

Preliminary studies revealed an accumulation of soluble salts in the lower horizons of both the sodium nitrate and the ammonium sulfate plots. This suggested that perhaps insufficient water was penetrating these soils to keep leached out of the root zone the salts brought in by irrigation water. Observations during the irrigation season of 1943 showed very marked decreases in the rate of water penetration in the ammonium sulfate and sodium nitrate plots.

In connection with an irrigation experiment on this same type of soil, Huberty and Pillsbury (4) found that heavy applications of ammonium sulfate applied in basins markedly reduced the water infiltration rate, whereas similar applications of calcium nitrate increased the infiltration rate, when compared with check plots receiving no fertilizer. In a series of special basin experiments in Kern County, California, where potato growers were experiencing difficulties with water infiltration, these same investigators (4) showed that both sodium nitrate and ammonium sulfate reduced the infiltration rate, whereas horse manure and gypsum, respectively, increased the infiltration rate, when compared with nontreated check plots.

In an effort to determine, if possible, what had occurred in the sodium nitrate and ammonium sulfate plots of the Citrus Experiment Station fertilizer plots, a detailed laboratory study was undertaken. The findings are reported in this paper.

BRIEF DESCRIPTION OF FERTILIZER EXPERIMENT

The layout and early history of this experiment are described elsewhere (1), as are also the effects of the first 12 years of differential fertilization on tree responses (7). Briefly, each trial plot consists of a single row of eight navel orange trees planted 20 feet apart. Guard rows consisting of alternate Valencia orange and grapefruit trees, planted 24 feet from the navel orange trees, separate the plots. There are four replicate plots per treatment.

The plots are furrow-irrigated by means of six straight furrows on each side of the plot trees. The soil surface directly beneath the drip of the trees is not furrowed and consequently does not receive irrigation water directly. Fertilizer is applied broadcast on the irrigated area only.

The fertilizer treatments of the plots reported in the present study are shown in table 1. All the fertilizers save manure are applied annually, in the spring. Gypsum is also applied annually, in the spring, at the rate of 1 ton per acre. Limestone, however, is applied once every 4 years at the rate of 4 tons per acre. When cover crops are grown, they usually consist of yellow bitter clover (*Melilotus indica*) and mustard (*Brassica nigra*), planted in the fall.

The soil on which the plots are laid out is classified on the soil map as Ramona

³Parker, E. R., Chapman, H. D., and Aldrich, D. G. Some effects of long-continued use of certain concentrated nitrogenous fertilizers and soil amendments. 1945. [Unpublished.]

loam but on the basis of mechanical analysis comes closer to a sand or sandy loam (see table 2). It is of old alluvial origin, with some evidence of moderate profile development. It is derived from granitic rock and contains more or less mica and other minerals and small gritty pieces of undecomposed and partly decomposed granite. The soil to a depth of 12 inches consists of a brown, rather friable, light-textured, sandy, gritty loam. It is very slightly reddish when wet. The substratum is a compact, gritty loam of varying thickness. The

TABLE 1
Source and amount of nitrogenous fertilizer applied

TREATMENT	PLOT NUMBER	TOTAL* FERTILIZER/ TREE 1927-1943	Total† fertilizer/acre 1927-1943
		<i>pounds</i>	<i>pounds</i>
Calcium nitrate + cover crop‡	D-32	146.19	18,952
Sodium nitrate + cover crop	D-52 K-14	159.23	20,643
Ammonium sulfate + cover crop	D-46 M-18	120.77	15,657
Sodium nitrate, gypsum, + cover crop	D-40 L-38	159.23 264.44	20,643 34,283
Ammonium sulfate, calcium carbonate, + cover crop	H-20 M-2	120.77 440.70	15,657 57,134
Urea + cover crop	F-50 M-12	54.36	7,047
Manure + cover crop	D-20 M-34	600.00	77,786

* Total amount added per tree from 1927-1943 inclusive (from 1927-1939, the fertilizer was applied at a rate to supply 1 pound nitrogen per tree annually; from 1940, the rate was trebled).

† This figure is obtained by multiplying fertilizer application per tree by 90.75 (trees per acre), and dividing by 0.70. The materials have been applied on only the irrigated area, which is about 70 per cent of the land.

‡ The cover crop on each plot is planted in the fall and disked under in spring.

entire area is of even topography, with a mild, uniform slope, and the surface soil is of uniform texture.

A mechanical analysis of a representative soil sample from the plots is shown in table 2, and a chemical analysis in table 3.

An average of 33 acre-inches per acre of irrigation water has been applied annually to the fertilizer plots since differential fertilization was begun in 1927. Rainfall has averaged about 11 inches a year.

The composition of the irrigation water, as shown by the average of 15 analyses made during the last 12 years, is as follows, in milliequivalents per liter: Ca,

2.43; Mg, 0.76; Na, 1.46; Cl, 0.63; SO₄, 1.03; HCO₃, 3.00. Total solids in this water averaged 346.3 p.p.m. The tap water used for the determination of permeability, aggregation, and macropore space in the present studies was of approximately the same composition.

TABLE 2
Mechanical analysis of soil from fertilizer plot D-32*

PARTICLE SIZE	PER CENT
<i>mm.</i>	
2.00-1.00	4.08
1.00-0.50	17.34
0.50-0.25	16.32
0.25-0.10	14.28
0.10-0.05	28.16
0.05-0.002	7.58
0.002	12.24

* Mechanical analysis made according to the method of Olmstead, Alexander, and Middleton (6).

TABLE 3
Analysis of soil from untreated fertilizer plot L-14
(Sampled in 1918)

CONSTITUENT	SAMPLE TO DEPTH OF 0-12 INCHES
pH	6.62
	<i>per cent</i>
SiO ₂	66.36
Al ₂ O ₃	20.04
Fe ₂ O ₃	3.52
TiO ₂	1.40
CaO	2.38
MgO	1.02
K ₂ O	1.52
Na ₂ O	1.91
MnO	0.11
P ₂ O ₅	0.10
C	0.39
N	0.08
CaCO ₃	0.00

MATERIALS AND METHODS

Soil samples

Except for determinations of macropore space, which were made on fresh samples of undisturbed cores drawn from the field, all data reported in this paper were obtained on air-dried soil which had been removed from the variously fertilized plots with a 3-inch augur. Although each treatment is replicated

four times throughout the orchard, only two plots of each treatment were sampled for this investigation. Through an oversight at the time of sampling, only one plot receiving calcium nitrate was sampled.

Eight systematically distributed borings were made in each plot at each of the following depths: 0-6, 6-12, 12-24, and 24-36 inches. The soil from the borings at each depth was composited and provided a sample of approximately 20 pounds. All samples were air-dried. The large lumps in each sample were broken down gently with a wooden roller, and the entire sample was then screened through a 2-mm. sieve.

Permeability

The permeability of the soil from each of the fertilizer plots was obtained by use of a percolation apparatus constructed from metal tubes 40.71 sq. cm. in cross-sectional area and 20 cm. in length.

One kilogram of soil was added to each tube by means of a spatula, to avoid excessive stratification. The soil was then compacted by dropping the tube 20 times from a 1-inch height to a steel plate. This method of compacting produced a soil column 17 cm. long. Variations from this length, when soil from different plots was used, were so small that the value 17 cm. was used in all subsequent calculations of permeability based on the Darcy equation (2) for flow of water through saturated soil.

After the aforementioned compaction, the tubes were placed upright in a tank of water and the soil was allowed to saturate by wetting from the bottom. Once the soils were saturated, the tubes were removed from the tank and attached by means of suitable connections to a reservoir of water maintained at constant hydraulic head. Though there are several methods of maintaining constant hydraulic head, the principle of the Mariotte flask (8) was employed on the apparatus used in this laboratory. This method of maintaining constant head avoids the continuous overflow of water at the influx end of the percolation apparatus, necessary for the constant-head methods, and avoids the use of excess water where the quantity of water of a particular base composition used for leaching is limited. A head of 52 cm. of water was used throughout the permeability study.

Aggregate analysis

The wet-sieve method of Yoder (10), with some modifications, was used to determine degree of aggregation.⁴

A 25-gm. sample of soil which had been passed through a 2-mm. sieve was spread evenly on the top sieve of a nest of four sieves containing nominal openings of 1.0, 0.5, 0.25, and 0.1 mm., respectively. The nest of sieves was tapped gently to reduce the quantity of soil on the top one and to bring about a better distribution of the sample on the sieves below. Particles that passed the finest sieve were dumped into the sieving tank.

⁴The authors wish to thank O. C. Magistad, director of the Regional Salinity Laboratory, U. S. Department of Agriculture, Riverside, California, for the use of the wet-sieving apparatus used in these studies.

The nest of sieves was next clamped into a sieve holder and was lowered slowly at an angle into the water in the sieving tank. This allowed the finer screens to wet gradually and prevented the entrapment of air bubbles which otherwise might be formed. The presence of the air bubbles reduces the effective sieving surface, particularly of the finer sieves, and introduces serious errors.

The quantity of water in the sieving tank was adjusted so that at the top of the sieving stroke the water level inside the top sieve dropped to the approximate level of the screen.

The soil on the sieves was allowed to slake for 1 hour and was then sieved for 30 minutes. The sieving apparatus was adjusted to raise and lower the sieves through a stroke length of $1\frac{1}{4}$ inches, at the rate of 24 strokes a minute.

Since the usual method of distinguishing between primary particles and aggregates is to make an analysis of a sample with and without dispersion, a second 25-gm. sample of soil was weighed out and dispersed according to the Bouyoucos hydrometer method for mechanical analysis. After the sample had been dispersed, it was washed on a nest of sieves containing the same nominal openings employed for measuring the amount of aggregates. The nest of sieves was placed in a sieving tank and sieved for 30 minutes along with the undispersed sample.

At the end of the sieving period the sieve nests were removed from the tanks and the particles on the sieves were oven-dried at 105° C. The weight of the particles remaining on each sieve was then obtained for subsequent calculations.

Macropore space

The procedure for determining noncapillary or macropore space was in principle the same as that described by Leamer and Shaw (5). The particular apparatus used was designed in this laboratory and has been found especially adaptable to pore-space measurements made in the range of 0 to 1,000 cm. of water tension.

Cores of soil of natural field structure, taken at depths of 1 to 4 inches, were obtained in 3- by 3-inch steel cylinders, by means of a sampling tube constructed for this purpose. The cylinders of soil fresh from the field were saturated with water by capillarity, weighed, and then clamped to a steel base which fits by means of a rubber-stopper connection into a Pyrex extraction flask. A steel cover plate with a $\frac{1}{8}$ -inch hole bored in the center to provide atmospheric pressure over the top of the sample was clamped over the cylinder of soil. A vacuum, equivalent to 40 cm. of water tension, was then applied to the extraction flask and was maintained by a constant-vacuum regulator.⁵ A 48-hour extraction period was usually sufficient to bring the sample to equilibrium. The amount of water lost was then measured and expressed as percentage by volume. This is considered to represent the percentage of macropore space in the undisturbed sample.

⁵Designed by George F. Liebig, Jr., of this laboratory.

Organic carbon

The organic carbon content of the soil from the various plots was determined by the Walkley-Black method (9) as modified by Joel Fletcher⁶ and the senior author of this paper.

A 3-gm. sample of soil which had been ground to pass a 100-mesh screen was weighed into a 250-ml. beaker. Ten milliliters of exactly 1 *N* potassium dichromate was pipetted into the beaker, and one drop of Aerosol⁷ was added from a dropping pipette. The suspension was stirred until wetting of the particles was complete. Twenty milliliters of concentrated sulfuric acid was run in from a dispensing burette, and the mixture was again swirled. The sample was then heated over a Bunsen flame until incipient fuming of the sulfuric acid occurred. Fuming occurs in about 1 minute at a temperature of approximately 150° C. Care must be exercised during heating, for too long heating results in higher

TABLE 4

Comparison of modified Walkley-Black and chromic acid-sulfuric acid oxidation method for determining organic carbon

SOIL NUMBER	CARBON CONTENT	
	Modified Walkley-Black method	Chromic-sulfuric acid method
	<i>per cent</i>	<i>per cent</i>
18560	0.35	0.36
19945	0.41	0.43
19946	0.33	0.33
19948	0.28	0.27
19949	0.21	0.22

temperatures and a reduction in titer of the dichromate. After cooling for a short while, the sample was diluted with water to a volume of about 150 to 175 ml. and was titrated with 0.5 *N* ferrous ammonium sulfate solution, the Gay equivalence point meter (3) being used to detect the end point of the titration.

The results of this method were checked against those obtained by a chromic acid-sulfuric acid combustion method in which the carbon dioxide evolved was accurately measured. The results of the two methods are shown in table 4.

Exchangeable bases

Exchangeable bases were determined by the ammonium acetate method. The organic matter in the leachate was destroyed by hydrogen peroxide and nitric acid treatments. Calcium was determined volumetrically after precipitation as the oxalate; magnesium, gravimetrically after precipitation as the quino-late; sodium, volumetrically after precipitation as the sodium uranyl acetate;

⁶Assistant soil technologist, Soil Conservation Service, U. S. Department of Agriculture, Tucson, Arizona.

⁷A wetting agent distributed by the Fisher Scientific Company, Pittsburg, Pa.

and potassium, gravimetrically after precipitation as the cobaltinitrate. Prior to leaching with ammonium acetate, water-soluble bases were removed from the soil samples by leaching with distilled water containing just sufficient ethyl alcohol to prevent dispersion. This extract was analyzed for soluble bases. The ammonia retained by the soil after leaching and washing with methyl alcohol to remove excess salt was determined by aeration and is considered to represent total base-exchange capacity.

RESULTS

A complete study was made of both chemical and physical properties of soil horizons at depths of 0-6, 6-12, 12-24, and 24-36 inches, respectively. As differences in horizons below the 6-inch depth were small, however, only the data for the surface horizon are given here.⁸

Physical changes

The determinations of permeability, percentage of water-stable aggregates greater than 0.1 mm., and macropore space of the soil are shown in table 5. In confirmation of field observations, it was found that the rate of water percolation through the sodium nitrate and ammonium sulfate soils was markedly less than that through the calcium nitrate soil. Where gypsum was applied along with sodium nitrate, or limestone with ammonium sulfate, permeability was not so poor as without these, but still was not so good, in the laboratory tests, as in the calcium nitrate soil. Urea appears to have decreased permeability somewhat over that of the calcium nitrate soil. The permeability of the manure soil is lower than that of the urea soil; but, on the other hand, so far as macropore space, percentage aggregates, and tree condition in the field are concerned, the manure soil is practically as good as the calcium nitrate soil. It is logical to believe that the hydration of organic colloids might reduce the rate of water movement despite other favorable physical conditions.

It appears likely that the reduced rate of water movement in the sodium nitrate and ammonium sulfate soils is due, in part at least, to a reduction in macropore space brought about by a certain amount of structural breakdown. It will be noted that, under conditions of wet-sieving, both of the aforementioned soils have decidedly fewer aggregates of particle size greater than 0.1 mm. than have the calcium nitrate, manure, or urea soils. The percentage aggregation is obtained by subtracting the percentage of material greater than 0.1 mm. found by mechanical analysis from that found by aggregate analysis. The data, as regards

⁸The cultural operations on the soil during the course of a year consist of disking in two directions in the spring to cut up and incorporate winter cover crops thoroughly. The irrigated area (from which the composite soil sample was drawn for study) is then furrowed out. Though practice has varied somewhat in past years, it has been customary, after the spring disking and furrowing, to harrow several times during the irrigation season to control weeds. After each harrowing, the plots are furrowed out again. It is evident, therefore, that the surface 4 to 6 inches of soil was thoroughly mixed from year to year, and that the chemical and physical measurements of the 0-6-inch horizon are those of a soil which has been stirred and mixed repeatedly.

aggregation, are remarkably consistent in the similarly treated plots, and repeated determinations in the laboratory gave highly consistent findings. There is no question, therefore, that structural changes in the direction of greater dispersion have taken place in the sodium nitrate and ammonium sulfate plots. This is reflected in the determination of macropore space. These two soils have the lowest percentage of macropores. It will be recalled that the determinations of macropore space were on fresh samples drawn from the field, whereas

TABLE 5

Permeability, aggregation, and macropore space of soils from differentially fertilized plots

PLOT NUMBER	LABORATORY* PERMEABILITY	WATER-STABLE AGGREGATES >0.1 MM.	MACROPORE SPACE†
		<i>per cent</i>	<i>per cent</i>
D-32	1.790	15.6	3.48
D-20	0.424	14.8	3.26
M-34	0.464	22.4	3.14
F-50	0.768	10.4	2.90
M-12	0.968	11.6	3.12
D-52	0.004	6.0	1.90
K-14	0.184	5.2	1.93
D-40	0.648	10.8	2.87
L-38	0.616	12.2	2.87
D-46	0.176	3.2	1.93
M-18	0.240	4.2	1.97
H-20	0.800	10.6	3.53
M-2	0.656	11.2	2.95

* Calculated according to Darcy's equation, $P = \frac{QL}{AH}$, where P = permeability; Q = cubic centimeters of leachate per hour; L = length of soil column; A = cross-sectional area of soil column in square centimeters; and H = hydraulic head, in centimeters.

† Pore space determined at tension of 40 cm. of water.

the permeability and aggregate data were obtained on air-dried composite samples brought in for laboratory study.

Chemical changes

In order to explain, if possible, the deterioration of soil structure in the sodium nitrate and ammonium sulfate plots, an investigation of the chemical properties of the various soils was undertaken. Determinations of organic carbon, water-soluble salts, and exchangeable bases were made.

Organic-carbon determinations on the surface soils of the plots under study are shown in table 6. In view of the variations between similarly treated plots,

the results show little if any difference save in the manure plots. Though organic matter is of unquestioned importance in relation to physical condition, the deterioration of structure in the sodium nitrate and ammonium sulfate plots is apparently not due to a lower organic matter content.

The exchangeable and water-soluble bases, base-exchange capacity, and pH values are shown in table 7. The exchange capacity of the soil is relatively low and is somewhat variable from plot to plot, ranging from 5.23 to 8.35 m.e. per 100 gm. of soil.

At first glance it might appear that, except for less exchangeable calcium in the ammonium sulfate soil, no significant changes have occurred in the base status

TABLE 6
Organic carbon content of soil from fertilizer plots
(Soil from 0-6-inch depth)

PLOT NUMBER	ORGANIC CARBON
	<i>per cent</i>
D-32	0.502
D-20	0.829
M-34	0.766
F-50	0.487
M-12	0.443
D-52	0.516
K-14	0.443
D-40	0.529
L-38	0.469
D-46	0.612
M-18	0.512
H-20	0.425
M-2	0.432

of the soils of the variously fertilized plots. In the sodium nitrate plots, however, there is a significant, though small, increase in replaceable sodium. Perhaps the most pertinent fact is that the calcium-sodium ratio in this soil is 8:1, whereas in the calcium nitrate soil it is 93:1. Reference to table 5 shows that the latter plot has the highest rate of water penetration and a high percentage of macropore space and of water-stable aggregates.

Though it would be premature to conclude that the lowering of the calcium-sodium ratio is entirely responsible for the structural changes noted, and for the consequent decreased water penetration, the data strongly suggest that this is one of the dominant factors. It will be recalled that the soils of the fertilizer plots have a low organic matter content and are frequently cultivated. It is not

unreasonable to suppose that but a small change in the distribution of the exchangeable divalent and monovalent cations sorbed by the clay fraction is required to promote structural deterioration.

Although it is likely, from the low pH of the ammonium sulfate plot, that calcium ions have been replaced by hydrogen ions, it does not seem logical to conclude that this exchange of ions is responsible for the structural changes noted, since hydrogen acts very much like calcium in promoting aggregation.

In considering other possible causes for the harmful effects of ammonium sulfate, the thought occurred that perhaps because of the low pH of this soil,

TABLE 7
Exchangeable and water-soluble bases in differentially fertilized plots

PLOT NUMBER	pH AT STICKY POINT	EX- CHANGE CAPACITY	EXCHANGEABLE BASES					WATER-SOLUBLE BASES				WATER-SOLUBLE BASES	
			Ca	Mg	Na	K	Ratio, Ca:Na	Ca	Mg	Na	K	Total	Ratio, Ca:Na
		m.e.*	m.e.	m.e.	m.e.	m.e.		m.e.	m.e.	m.e.	m.e.	p.p.m.	
D-32	6.9	6.98	6.56	0.52	0.07	0.20	93:1	1.42	0.03	0.08	0.08	615.2	15.4:1
D-20	7.1	8.01	6.53	0.84	0.15	0.40	44:1	0.61	0.18	0.20	0.40	395.4	2.6:1
M-34	7.3	8.35	7.03	0.66	0.15	0.51	47:1	0.59	0.18	0.22	0.59	404.3	2.3:1
F-50	6.7	6.97	5.05	0.66	0.24	0.51	21:1	0.57	0.12	0.14	0.01	321.6	3.5:1
M-12	6.5	5.59	3.98	0.30	0.23	0.23	17:1	0.56	0.09	0.14	0.01	310.4	3.5:1
D-52	7.4	7.30	5.80	0.97	0.77	0.36	8:1	0.54	0.01	2.24	0.08	1249.1	0.2:1
K-14	7.5	5.23	4.52	0.51	0.54	0.23	8:1	0.40	0.06	0.90	0.06	588.6	0.4:1
D-40	7.4	8.00	6.89	0.61	0.10	0.40	69:1	3.34	0.02	1.74	0.12	2106.1	1.6:1
L-38	7.4	6.33	5.28	0.57	0.26	0.22	20:1	1.81	0.15	1.58	0.02	1491.6	1.0:1
D-46	4.1	8.30	3.86	0.50	0.22	0.44	17:1	0.41	0.12	0.23	0.10	302.6	1.5:1
M-18	4.0	5.40	2.67	0.30	0.27	0.31	9:1	0.25	0.12	0.18	0.02	515.1	1.2:1
H-20	7.3	5.35	4.26	0.36	0.25	0.28	17:1	3.90	0.32	0.14	0.02	1702.0	24.2:1
M-2	7.3	5.50	4.51	0.45	0.25	0.39	18:1	3.25	0.32	0.14	0.02	1442.0	20.2:1

* M.e. in this table = per 100 gm. soil.

the applied ammonia was not nitrifying properly. A determination of absorbed ammonia was therefore made in this plot and in the several other plots for comparison. A surprising amount of exchangeable ammonium was found in the soil of the ammonium sulfate plots. The plots receiving ammonium sulfate alone showed 3.44 and 2.87 m.e., respectively, of ammonium per 100 gm. of soil, whereas the plots receiving calcium nitrate alone or ammonium sulfate plus calcium carbonate showed only 0.28 and 0.22 m.e. of ammonium, respectively. Inasmuch as the ammonium ion has a dispersing effect similar to sodium, though perhaps not so great as sodium, the reason for the poor physical condition of the ammonium sulfate plot is apparent.

It will be noticed that there are material differences in the total water-soluble bases of these various soils, and, as might be expected, in the ratio of calcium to sodium. Undoubtedly, the variable electrolyte content is not without influence on aggregation and water movement, but its importance cannot be evaluated without further study.

DISCUSSION

The results of this study are of interest from many points of view. The most surprising feature is the discovery that the well-known acidifying effect produced on a soil by the continued use of ammonium sulfate may result in a sufficient accumulation of exchangeable ammonium seriously to impair the physical condition of the soil. It was formerly considered that the acidifying effect of ammonium sulfate on the irrigated soils of arid and semiarid regions could be largely ignored, for with naturally neutral or alkaline soils and use of alkaline irrigation water, it was thought that the acidity produced would be neutralized. As a matter of fact, our calculations show that the amount of irrigation water applied to the ammonium sulfate plots contained more than enough bicarbonate to neutralize the entire acidifying potential of the ammonium sulfate applied. Studies of these plots from time to time have shown, however, that the ammonium sulfate plots have become more and more acid. Whatever the true explanation, it is certain that the outgo of basic material by leaching has been hastened by the application of ammonium sulfate. That the acidity in the surface soil might eventually develop to a degree sufficient to prevent or seriously retard nitrification had not previously occurred to us. The present study clearly confirms this possibility. Impairment of soil structure is one, though by no means the only, ill effect which may ensue.

With reference to sodium, if we attribute the poor condition of the sodium nitrate plot to lowering of the calcium-sodium ratio, it is apparent that very serious impairment of water penetration and other soil characters may arise from rather small increases in exchangeable sodium. It will be recalled that the sodium nitrate soil with a base-exchange capacity of 7.3 m.e. per 100 gm., contains less than 1 m.e. of sodium. Many factors, of course, enter into the question of how much exchangeable sodium, or what proportion of the exchange capacity, must be converted to the sodium form before poor structural conditions become manifest. Among the more important factors are the ultimate particle-size distribution in the soil, the amount of organic matter, the electrolyte content of the soil solution, the amount and kind of cultivation practiced, and the moisture condition prevailing at the time the soil is tilled. Some soils are much more vulnerable to structural deterioration than others; the soil of the experimental field of the University of California Citrus Experiment Station probably falls into the former category.

Another point should be noted, namely, that deterioration of soil structure to date is confined to the upper 6 inches of soil. Below this level no evidence of impairment in water penetration, structure, or chemical make-up was observed. The striking deterioration of tree condition in sodium nitrate and ammonium

sulfate plots serves to emphasize the great importance of this surface horizon. Actually, the bulk of the root system is found below this layer, but both water and air must move freely through it; hence no matter how favorable the root zone may be, the condition of the surface soil is vital.

SUMMARY

A study has been made of the effects of several nitrogenous fertilizers and soil amendments on the physical and chemical properties of an irrigated soil in plots of a long-term fertilizer experiment.

Marked physical and chemical changes are shown to have occurred after 16 years of treatment, the last 4 of which involved the application of large amounts of fertilizer. The rate of water percolation through soil fertilized with sodium nitrate or with ammonium sulfate is markedly less than that through soil fertilized with calcium nitrate. If gypsum is applied with the sodium nitrate, and limestone with the ammonium sulfate, percolation is not so poor as without these, but it is still not so good as in the calcium nitrate plot. Urea appears to have decreased permeability somewhat over that in the calcium nitrate plot, and manure appears to have decreased it still more than urea, though the manure plots seem to be in excellent physical condition on the basis of aggregate and macropore-space analyses.

It appears likely that the reduced rate of water movement in the sodium nitrate and ammonium sulfate soils is due, in part at least, to a reduction in macropore space brought about by a certain amount of structural breakdown. Laboratory measurements of structural breakdown, by means of macropore-space analyses, produce data from all treatments, with the exception of the manure plots, which are well correlated with percolation data.

Chemical data obtained on the various plots suggest that the poor physical condition of the sodium nitrate plots is due to an unfavorable calcium-sodium ratio. The poor physical condition of the ammonium sulfate plots is apparently due to the dispersing action of the ammonium ion, which builds up in the exchange complex as a result of the reduced ability of soil organisms to nitrify the ammonium at the low pH produced by the continued application of ammonium sulfate. The addition of gypsum with the sodium nitrate maintains a calcium-sodium ratio which is conducive to structural stability. The addition of limestone with the ammonium sulfate neutralizes the acidity produced by the application of this fertilizer; soil organisms are then able to nitrify the sorbed ammonium and thus prevent its build-up in the exchange complex in sufficient quantities to cause structural deterioration.

REFERENCES

- (1) BATCHELOR, L. D., PARKER, E. R., AND McBRIDE, R. 1928 Studies preliminary to the establishment of a series of fertilizer trials in a bearing citrus grove. Calif. Agr. Exp. Sta. Bul. 451. (Out of print.)
- (2) DARCY, H. 1856 Les Fontaines publiques de la ville de Dijon. Victor Dalmont, Paris.
- (3) GAY, J. R. 1939 Determination of electrometric equivalence points. *Indus. and Engin. Chem., Analyt. Ed.* 11: 383-386.

- (4) HUBERTY, M. R., AND PILLSBURY, A. F. 1941 Factors influencing infiltration rates into some California soils. *Amer. Geophys. Union Trans.* 1941: 686-697.
- (5) LEAMER, R. W., AND SHAW, B. 1941 A simple apparatus for measuring noncapillary porosity on an extensive scale. *Jour. Amer. Soc. Agron.* 33: 1003-1008.
- (6) OLMSTEAD, L. B., ALEXAMDER, L. T., AND MIDDLETON, H. E. 1930 A pipette method of mechanical analysis of soils based on improved dispersion procedure. U. S. Dept. Agr. Tech. Bul. 170.
- (7) PARKER, E. R., AND BATCHELOR, L. D. 1942 Effect of fertilizers on orange yields. Calif. Agr. Exp. Sta. Bul. 673.
- (8) PIPER, C. S., AND OERTEL, A. C. 1941 Silica and pyrex glass stills with automatic constant-pressure feeds. *Indus. and Engin. Chem., Analyt. Ed.* 13: 191-192.
- (9) WALKLEY, A., AND BLACK, I. A. 1934 An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Sci.* 37: 29-38.
- (10) YODER, R. E. 1936 A direct method of aggregate analysis of soils and a study of the physical nature of erosion losses. *Jour. Amer. Soc. Agron.* 28: 337-351.

THE WATER TABLE, EQUIPOTENTIALS, AND STREAMLINES IN DRAINED LAND: II

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The general nature of the problem to be attacked, and the methods involved, have been described in an earlier paper (1), which will be referred to here as "part I." Briefly, the shape and position of the water table and the water-flow paths in pervious land must be investigated for various circumstances of soil permeability and depth, rainfall intensity, and artificial drainage. This is accomplished by constructing an electric analogue of the particular hydrodynamic problem by a process of trial and error, and on this analogue plotting the electric equipotentials and streamlines and tracing the "water table." By means of a conversion factor the equipotentials may then be labeled in the appropriate hydrodynamic terms, the scale first having been settled. Part I dealt with those points which naturally called for first attention and, in particular, demonstrated the inadequacy of current theory based on the Dupuit assumptions, which have been sufficiently criticized by Muskat (6, p. 359 *et seq.*). The purpose of the present communication is to discuss (a) the perturbing effect of holes such as are commonly used in attempts to locate the water table in the field, (b) the relative efficacy of flooded and empty drains, (c) the effect of piping and filling in a previously open trench, and (d) the role of the capillary fringe. The assumption continues to be made, as in part I, that all conditions are strictly uniform in the direction of the drain lines, so that the problem is reduced to one of two dimensions, and the electric analogue is in all cases a sheet conductor cut to the appropriate shape and with a suitable array of electrodes. It is further assumed throughout that rainfall is steady and is uniformly distributed over the soil surface and that the streamlines in the upper or unsaturated zone are vertical straight lines.

EXPERIMENTAL RESULTS

Perturbation due to observation pits

The condition of uniformity in the drain-line direction implies that our observation "hole" is a long slit trench parallel with the drain lines. Provided there is free entry for water through all parts of the walls, that part of the slit which is full of water is an equipotential body which imposes its potential on the water in the immediately contiguous soil. The electric analogue of the ground water being a sheet of relatively low electrical conductivity representing a cross section perpendicular to the drain lines, the analogue of the observation slit is a strip of material of relatively high conductivity, such as metal foil, scaled to repre-

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sent the cross section of the slit, and cemented with a conducting cement to the sheet conductor in such a position as to represent to scale that part of the slit below the water table. The water table must, of course, be located by trial and error

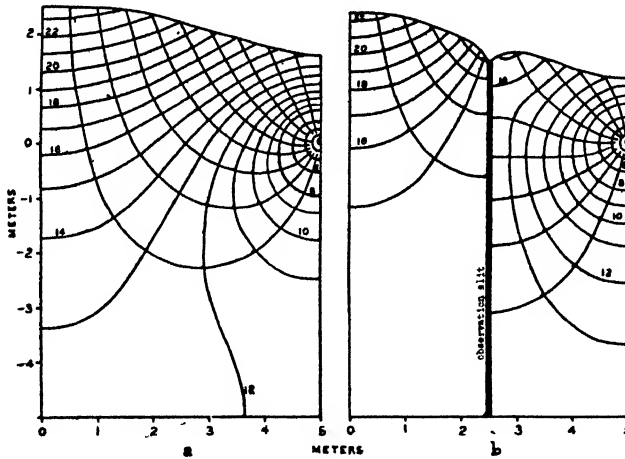


FIG. 1. DISTORTION OF THE WATER TABLE INTRODUCED BY AN OBSERVATION SLIT HALFWAY BETWEEN A DRAIN AND THE MIDPOINT BETWEEN DRAINS

a. Without slit; b. With slit. The equipotentials in all stream pictures are labeled in units of 10^4 ergs per centimeter

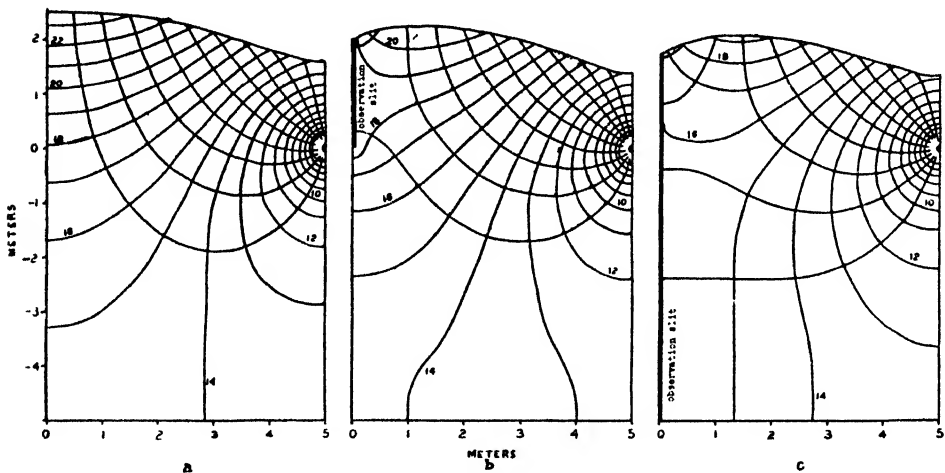


FIG. 2. SAME AS FIGURE 1, BUT WITH OBSERVATION SLIT MIDWAY BETWEEN DRAINS

a. Without slit; b. With slit reaching to drain level; c. With slit reaching to impermeable bed

in the presence of the imposed equipotential. Reference to figures 1b, 2b, 2c, and 3b will make this description clearer. For the sake of simplicity the drains have been assumed to be just full of water, so that the drain perimeter may be

taken as our zero equipotential; surfaces of seepage have been avoided. Further, for the sake of simplicity introduced by symmetrical conditions, the drainage system has been assumed, as in part I, to comprise parallel equidistant drain lines of uniform depth and separation, so that it is sufficient to demonstrate the stream picture between two parallel vertical planes, one through a drain line and the other midway between this drain line and its neighbor. The experiments were carried out on conducting sheets 10 cm. wide and have been interpreted in all the published figures to a scale of 50 to 1, giving a drain separation of 10 m.

Figure 1a shows the stream picture for a drain diameter of 11.5 cm. and with a depth of 5 m. of pervious soil below drain level. The water-table height was chosen arbitrarily to be 250 cm. above drain centers at a point midway between neighboring drain lines, the ratio of rainfall intensity to soil permeability being thus arbitrarily defined (see part I). Figure 1b shows the effect on the stream picture of digging a narrow slit trench at a distance $d/4$ from a drain line (where

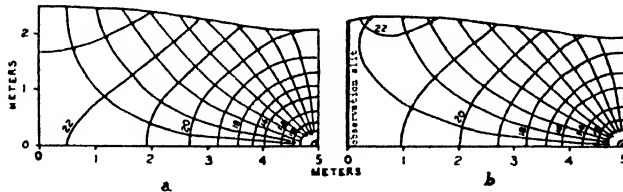


FIG. 3. SAME AS FIGURE 2, BUT WITH SHALLOW SOIL: DRAINS RESTING ON THE IMPERMEABLE BED

d is the drain separation) and reaching down to the impervious bed, all other factors remaining constant. Figures 2a and 2c similarly show the modification introduced by a slit midway between drain lines. Since it may be argued that in practice there is little point in sinking observation pits below drain level, at least where it is known that natural drainage is negligible, figure 2b is presented to show the modification at the intermediate stage of perturbation where the slit reaches only to drain level. Again, figures 3a and 3b show the effect when the soil is shallow, so that the drains rest on the impervious bed, the observation slit being, as before, midway between drain lines.

Relative efficiency of flooded and empty drains

Discussion of the effect of excess water in a drain usually turns on such mechanical aspects as the danger of bursts if a considerable back pressure is permitted or the danger of silting if stagnant water is retained. We are concerned here only with the effect on the water-table, assuming the entire mechanism to be in good order. Figure 4a shows the stream picture for a full drain, again with an arbitrarily chosen water-table height of 250 cm. above drain centers at the midpoint. With the drain empty of water, as could be arranged by laying it with sufficient fall, the stream picture is as shown in figure 4b. The drain perimeter is no longer an equipotential; the free water level is now at the floor of the drain,

and the remainder of the drain surface is a surface of seepage; hence a word of explanation of the preparation of the electric analogue is called for. The potential ϕ as defined in part I leads to

$$\phi = p + gph \quad (1)$$

where p is the hydrostatic pressure, h is the height above a chosen datum level, g is gravitational acceleration, and ρ is the density of the water. The datum level throughout is chosen to be that of the free surface of water in the drain, and the pressure datum to be atmospheric pressure; hence the free water surface in the drain is the zero equipotential, both p and h being zero. With the drain just full, the free surface being at the roof, the whole drain cross section is the zero equipotential, since p is everywhere equal to $-gph$; but with the free surface

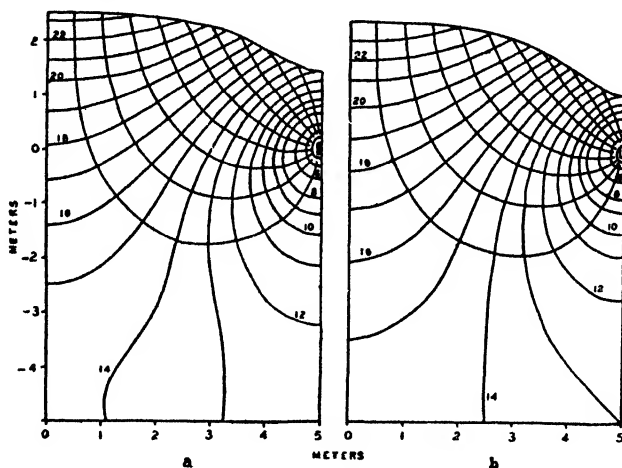


FIG. 4. LOWERING OF THE WATER TABLE PRODUCED BY LOWERING THE LEVEL OF WATER IN THE DRAINS

a. Drain full; b. Drain empty

at the floor, only the floor constitutes the zero equipotential. The remainder of the drain surface being a surface of seepage, p is everywhere zero, so that

$$\phi = gph \quad (2)$$

which is the same condition which holds at the water table, where also p is zero. Hence the electric analogue of the drain is an electrode, to scale, the lowest part of which is the zero equipotential and over the remainder of which a potential fall is maintained so that the potential V at any height h above the drain floor is given by

$$V = Ah \quad (3)$$

where A is the same constant as applies to the water table analogue. It is impracticable to maintain along a conductor a potential which is proportional to the vertical height unless that conductor is rectilinear; this accounts for the

rectangular drain section chosen for this experiment. The base and roof of the drain were represented in the analogue by copper wire conductors of diameter 0.25 mm., and the vertical sides, by wires of eureka resistance alloy of diameter 0.15 mm. The current passed through the system to maintain the required potential fall along the eureka wire was obtained from the battery that supplied all the other current required in the analogue (see part I), and was controlled by a separate rheostat so that equation (3) was satisfied simultaneously with the other necessary conditions. This analogue of a surface of seepage has been used by Wyckoff and Reed (10) in solving problems relating to seepage through dams but is rather troublesome on the small scale inherent in our problem.

Effect of piping and filling in a trench

The annual cleansing of open ditches is an important item of maintenance, which is commonly regarded as, at best, a necessary evil, and there is a very real temptation to pipe ditches and to fill them in. Circumstances also arise where it

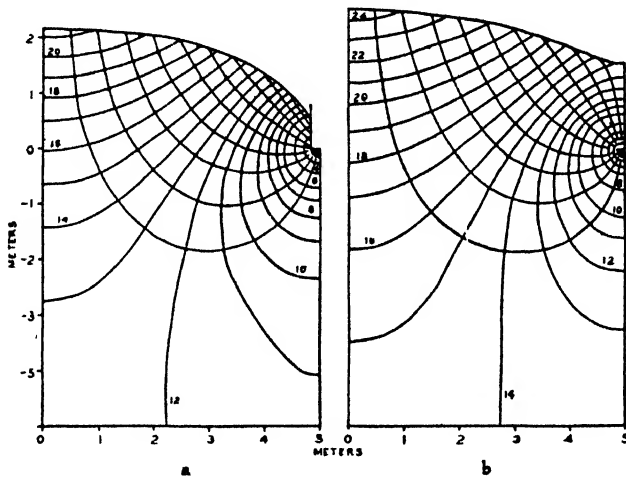


FIG. 5. RISE IN THE WATER TABLE CAUSED BY PIPING AND FILLING A DITCH

a. Open ditch with surface of seepage; b. Ditch filled, with pipe of same carrying capacity

is desirable to run two or more small fields together, necessitating the elimination of intervening ditches. Where the piping and filling operation is properly done, and the ditch is mainly a water conduit rather than itself constituting an effective drain, little harm may result, although there is always the danger that need for maintenance is only hidden, not removed. Where, however, the ditch is itself an effective drain, there is a clear need to investigate the effect on the stream picture of the piping and filling operation. Again for the sake of simplicity we assume a system of parallel equidistant ditches, to be replaced by a system of parallel drain lines similarly located and of equal water-carrying capacity.

Figure 5a presents the stream picture for a ditch with vertical sides; this

impracticable form does not impair its usefulness in demonstrating the effect. The width of the ditch is 30 cm., and the hemicylindrical floor is just filled with water to the horizontal diametral plane. The surface of seepage was represented in the electric analogue in the way described in the preceding section. When the ditch is piped and filled so as to give uniform permeability with the surrounding soil, as would be the case in practice after a period of settling, the stream picture for the same rainfall intensity is as shown in figure 5b. The unusual hemicylindrical form of drain pipe was adopted so that the same electrode could be used for the zero equipotential in both figures 5a and 5b, thus ensuring the minimum interference with the analogue between experiments and the maximum constancy of conditions other than that being deliberately varied. The water-carrying capacity is clearly identical in both cases.

Role of the capillary fringe

The use of the soil moisture characteristic (*i.e.*, the graph of moisture content plotted against hydrostatic pressure) to obtain the pore-size distribution is now a well-known procedure. A soil with not too great a range of pore sizes has a

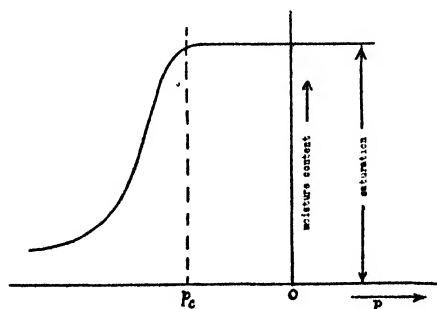


FIG. 6. SOIL MOISTURE CHARACTERISTIC TO ILLUSTRATE THE CONDITIONS DEFINING THE CAPILLARY FRINGE

moisture characteristic of the type shown in figure 6. There is a finite range of pressures less than zero for which the soil is practically saturated, but with still lower pressures there is appreciable emptying of the pores. The lower limiting pressure, p_c , for saturation is more or less sharply defined, depending on the soil. Hence if we take a vertical soil column in which the hydrostatic pressure decreases as height increases, starting with some positive value at the bottom, then there will be some height at which the pressure is zero; here lies the water table. The soil will continue to be perceptibly saturated to some greater height at which the pressure is p_c , and thereafter will decrease in moisture content with more or less rapidity. The zone between the water table and the upper limit of saturation is known as the capillary fringe, and its boundaries are defined by the pressure conditions

$$\left. \begin{array}{l} p = 0 \text{ at the lower boundary} \\ p = p_c \text{ at the upper boundary} \end{array} \right\} \quad (4)$$

If the moisture characteristic shows no well-defined limit p_c for saturation, then of course there is no well-defined boundary to the capillary fringe, which can then only be defined arbitrarily. It has been thought desirable to set out this statement in full, since Wyckoff, Botset and Muskat (9), in their illuminating pioneer work showing radial streaming in the capillary fringe above a well system, have asserted that the condition at both boundaries is $p = 0$. In the light of the above considerations, our assumption so far that the water table is the upper boundary of the relatively highly permeable region because it is the upper boundary of saturation is not in general valid; only in a very coarse-grained soil will the capillary fringe be of negligible thickness. In order to see the extent

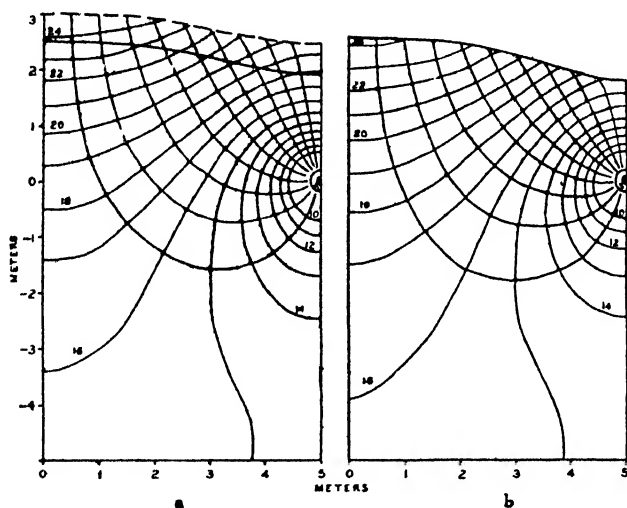


FIG. 7. NEGLIGIBLE ERROR INTRODUCED IN ESTIMATING THE WATER TABLE IF THE CAPILLARY FRINGE IS IGNORED

- a. Fringe taken into account (broken line represents upper boundary of capillary fringe);
 b. Fringe ignored

of the error which may be made by ignoring this fringe, we must first see how to take it into account in the electric analogue.

The potential function takes the values

$$\begin{aligned}\phi_{wt} &= gph & \text{at the water table and} \\ \phi_{cf} &= gph + p_c\end{aligned}\tag{5}$$

at the upper boundary of the capillary fringe (cf), where p_c is less than atmospheric and therefore negative on our scale. The upper boundary of the capillary fringe, and not the water table, is the boundary between the lower region of high permeability and the upper region of lower permeability, and is therefore the lower boundary of the zone in which we have assumed the streamlines to be vertical. We must therefore adjust the shape of the sheet conductor and the

current input representing rainfall so that the horizontal distribution of current is uniform over the locus of points satisfying the equation

$$V = Ah - C \quad (6)$$

where C is a positive constant, simulating the pressure p_c of equation (5). This locus then represents the upper boundary of the capillary fringe while the locus of points satisfying equation (3) represents the water table.

In figure 7a is shown the stream picture for a case in which the capillary fringe was taken into account. The water-table height was, as usual, arbitrarily chosen to be 250 cm. at the midpoint, thus fixing the constant A , and the thickness of the capillary fringe was arbitrarily chosen at the same place to be the large but reasonable value of 50 cm., thus fixing the value of C . When the scale of conversion from the electric analogue to the hydrodynamic problem is decided, the value of p_c emerges with the general solution. Figure 7b shows the stream picture for the same case when the capillary fringe is ignored. Figures

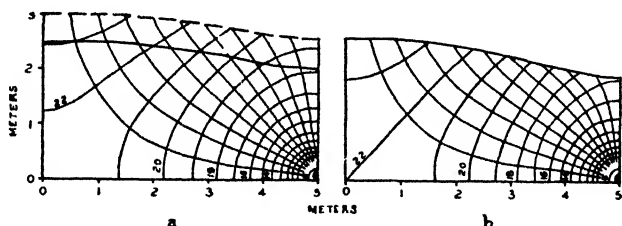


FIG. 8. SAME AS FIGURE 7, BUT WITH SHALLOW SOIL; DRAINS RESTING ON THE IMPERMEABLE BED

8a and 8b show a similar comparison with shallow soil, the drains being laid on the impervious bed.

DISCUSSION

It is true that the underlying assumption that the streamlines in the upper or unsaturated zone are vertical has not been verified, although it was shown in part I to be not unreasonable and has, in fact, underlain all previous work of a similar nature. It is not beyond the capacity of the electrical method to investigate the unsaturated zone, and studies to this effect have been begun. The process of successive approximation is, in this case, rather troublesome, however, and if we were not to assume the verticality of the upper streamlines, progress would be rather slow. It is certainly a simple matter to demonstrate the circumstances in which the assumption is strictly valid. In any of the stream pictures shown here or in part I, let the equipotentials be continued from their junctions with the water table (or more properly the upper boundary of the capillary fringe, where this is shown) as horizontal straight lines in the upper zone. The streamlines are therefore vertical straight lines in this zone. By equation (2) or (5), whichever is applicable, the equipotentials are equidistant in the upper zone, while the streamlines are equidistant by hypothesis, the rain-

fall being assumed to be uniformly distributed on the soil surface. Hence the permeability in the upper zone is uniform throughout, and turns out to be about one fifth that of the saturated zone. In general, however, it may be conceded that the streamlines in the unsaturated zone may depart somewhat from the truly vertical, and individual stream pictures may require some modification on that account, but it is unlikely that *comparisons* of the type discussed here will be much affected.

In figures 1a to 3b those streamlines which do not extend from the water table, but issue from the slit, were drawn rather by guesswork, to produce the most reasonable picture, uniform permeability being assumed. The difficulty is, of course, that though they are undoubtedly streamlines, they cannot be labeled with certainty and cannot be guaranteed to be true continuations of the streamlines which leave the water table to enter the slit on the other side. The immediately important factors, the shape and height of the water table, are truly given. It is at once obvious that the effect of the slit is profound; the water table is everywhere lowered even though the slit is not a true drain, insofar as no outfall is provided. In practice, a bore hole and not a long slit is used. Though undoubtedly the perturbation of the water table is then much more localized, it must still be of major significance at the observation point itself, and this is the point of immediate importance, at which information is being sought. The indicated level of the water table in such cases can have but little relation to the level sought, namely, the unperturbed level before the bore hole was sunk. The only case in which error does not arise is that in which the equipotentials are already vertical, for then the superimposed equipotential merely confirms the pre-existing one. Sunken tubes with impermeable walls, of the type used by Christiansen (2), are not open to this objection, but they are potential-measuring devices; and therefore, though the potential field may be traced reliably, the water table is not, and does not purport to be, directly indicated.

The effect of lowering the level of water in the drains, as shown in figures 4a and 4b, is more pronounced immediately over the drain lines than at some distance; the shape of the water table is changed. In practice, however, we are mainly concerned with the maximum height of the water table, midway between neighboring drain lines, and we see that this is lowered by an amount approximately equal to the lowering of the water in the drains.

The result of piping and filling a ditch seems to be rather important, as shown in figures 5a and 5b. Although the free water level in the drains is the same in each case, the water table is everywhere markedly lower when the drain is an open trench, which allows entry of water through an extended surface of seepage, than when it is a buried pipe. The shape of the water table is also much modified by piping and filling, the consequent rise being greater over the drain lines than at the midpoint. It is not possible, in fact, to locate very precisely the junction between the water table and the surface of seepage in an open trench by the electrical method, since this point can only be recognized by its satisfying equation (3), which equation is, of course, satisfied everywhere on the surface of

seepage. This junction is drawn in figure 5a by extrapolation, aided by an analysis of the shape of a free surface given by Shaw and Southwell (7), who showed that where the water table is also a streamline, it approaches a vertical surface of seepage with rapid curvature and joins tangentially. Their analysis may be extended to cover our more general case.

In figure 9 let P be any point on the water table, of which QPR is a cross section, and let n be the outward normal at P . Let h and x be the vertical and horizontal coordinates respectively, and let distance measured along QPR be s . Then the direction cosine dx/ds of the water table equals the direction cosine dh/dn of the normal. Let rainfall be uniformly distributed with intensity

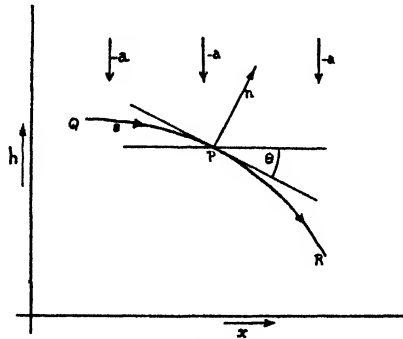


FIG. 9

$-a$ per unit horizontal surface (the minus sign allowing for the downward direction so that a is positive). We have

$$dx/ds = dh/dn = \cos \theta = l, \text{ say.} \quad (7)$$

The rate of arrival of water at P , per unit area of water table, is therefore $-la$. Hence

$$d\phi/dn = la/k \quad (8)$$

where k is the permeability, which was written P_w in part I, equations (8) and (9).² From equation (1) we have

$$d\phi/dn = dp/dn + g\rho(dh/dn) \quad (9)$$

Substituting from (7) and (8), we have

$$la/k = dp/dn + g\rho l \quad (10)$$

QPR is an isobar (p is everywhere zero), therefore $\text{grad } p$ is directed along n , and

$$dp/dh = l(dp/dn) \quad (11)$$

$$= l^2(a/k - g\rho) \quad (12)$$

² In those equations, ΔV should have been written $\Delta\phi$.

At the surface of seepage p is zero, and therefore, where this surface is vertical, we have

$$dp/dh = 0$$

Hence at the junction of the water table with the surface of seepage, l is zero, and the water table is therefore vertical, *i.e.*, it joins the surface of seepage tangentially.

Leaving this point and turning to the capillary fringe, we see that figures 7 and 8 show the water table arrived at to be much the same whether or not a capillary fringe of considerable thickness is taken into account. Neglect of this fringe causes a slight overestimation (by about 5 cm.) of the height of the water table at the midpoint and a somewhat greater underestimation (by about 10 cm.) over the drain lines. The capillary fringe is not of precisely uniform thickness throughout, but it does not vary by more than 5 per cent from the mean. The value of p_c , calculated by means of equation (5), is $-36,200$ dynes per square centimeter (-36.9 cm. of water) in figure 7a and $-43,500$ dynes per square centimeter (-44.3 cm. of water) in figure 8a. In both cases the magnitude of p_c is, of course, less than 50 cm. of water (the approximate thickness of the capillary fringe) by an amount required to maintain viscous flow through the fringe.

These general conclusions about the capillary fringe appear at first sight to be at variance with those of Hooghoudt (5), and the discrepancy must be examined. It is obvious that when flow is predominantly horizontal, as in seepage through earthen dams, any addition to the vertical thickness of the conductor, such as is afforded by the fringe, must have effect in reducing the resistance to flow, yielding greater flow for the same pressure conditions. Wyckoff, Botset and Muskat (9) have shown such an effect for radial streaming in the capillary fringe. In our case, however, the flow is seen to be predominantly vertical in the zone in question, and therefore an additional height of conductor carries with it an *increase* of resistance to flow, but with a compensating addition to the potential at the upper boundary; we have an extension both of the conductor and of the potential field, and the overall effect is to leave the flow rate for a given water table, or *vice versa*, almost unaffected. Hooghoudt's experiments employed ill-defined conditions. He studied the flow to drains laid in a sand-filled tank which was initially saturated nearly to the surface and then allowed to drain away without replenishment. The falling water table was therefore not a streamline, and distribution of flux at the water table was neither controlled nor precisely known. It could not legitimately be assumed to be uniform, as in our case, and in fact the evidence of the water table sequences shows approximate uniformity of flux only during part of the time. Nevertheless, the equations applied were developed for the case of steady, uniformly distributed rainfall and were based on the Dupuit assumptions. When the water table was low, agreement between theory and experiment was poor unless the thickness of the capillary fringe was taken into account. It happens that it was just in these circumstances of low water table that the curves indicated the nearest approach to horizontal stream-

ing, the water table descending much more rapidly at the midpoint than over the drains. Hence even if we admit the approximate validity of the formulas used [and Muskat (6, 359 *et seq.*) grants that formulas based on the Dupuit assumptions achieve fortuitous agreement with experiment, and even with more soundly based theories, surprisingly often] it cannot be said that Hooghoudt's important direct experiments are in conflict with those described here.

Finally, it may be fitting to discuss the place of the method of electric analogues in the general attack on drainage problems. Alternative lines of attack are (a) the direct study of soil water, either in the field or by models, (b) the analytical mathematical approach, and (c) what may be called experimental mathematics (3; 4; 6, p. 237 *et seq.*; 7; 8). The first involves measurements of relatively low precision, and controlled conditions cannot be achieved without considerable expense. Nevertheless, the final appeal must be to such methods, since in no other way can the conditions actually occurring in the field be studied. Taking (c) next, and referring in particular to Shaw and Southwell's (7) method of relaxation of restraints, we encounter in our problem the difficulty of getting started. The method replaces the uniform sheet with a lattice of points and Laplace's equation with a difference equation, and starts with a known potential distribution over parts of the boundary. The potentials (or pressures, which also are harmonic) are then computed for the remaining lattice points by a process of reiterated correction. In the earthen dam problems which Shaw and Southwell attacked, the potential distribution was known initially over the whole of the inflow and outflow faces, but in our problem it is known only over the minute portion of the whole boundary comprising the drain surface and one arbitrarily selected point on the water table. It is not to be questioned that numerical computation is in the end more accurate than the electrical method, although for practical purposes the latter is likely to be accurate enough. A weightier advantage of numerical computation is that it is independent of experimental techniques such as the preparation of uniformly conducting sheets, which is at best an uncertain business. Where the greatest accuracy is desired, it may be that the best use of the electric analogue is to provide a satisfactory starting point for further numerical computation.

As regards rigid analysis of the problem, we may consider the hodograph method, reviewed at some length by Muskat. The hodograph is the transformation in the (u, v) plane of the physical system in the (x, h) plane, where u and v are respectively the components of the flow velocity in the x and h directions. The analytical difficulties of the method are formidable, and our problem still awaits solution, but even if it should yield, the electric analogue would still be the most convenient way of depicting the streamlines within the boundaries as found mathematically.

The point of the hodograph is that a free surface, which cannot be located in the (x, h) plane until the problem is solved, may be represented at once in the (u, v) plane. Previous problems attacked by this method having been confined to the case where the free surface is also a streamline, it is the purpose of the

remainder of this brief section to show the nature of the hodograph of a water table on which rain is incident, this being the necessary first step in the solution of the problem.

Referring again to figure 9, we have, at the water table, where p is everywhere zero,

$$d\phi/dn = (a/k) \cos \theta \quad (13)$$

$$d\phi/ds = g\rho(dh/ds)$$

$$= g\rho \sin \theta \quad (14)$$

Hence
$$d\phi/dx = (g\rho - a/k) \sin \theta \cos \theta \quad (15)$$

and
$$d\phi/dh = (a/k) \cos^2 \theta + g\rho \sin^2 \theta \quad (16)$$

Since and
$$\left. \begin{aligned} u &= -k(d\phi/dx) \\ v &= -k(d\phi/dh) \end{aligned} \right\} \quad (17)$$

we have, by substituting for $d\phi/dx$ and $d\phi/dh$ and eliminating θ

$$u^2 + v^2 + v(a + k g \rho) + a k g \rho = 0 \quad (18)$$

which is the equation of a circle in the (u, v) plane with radius $(k g \rho - a)/2$ and with its center at the point $[0, -(k g \rho + a)/2]$.

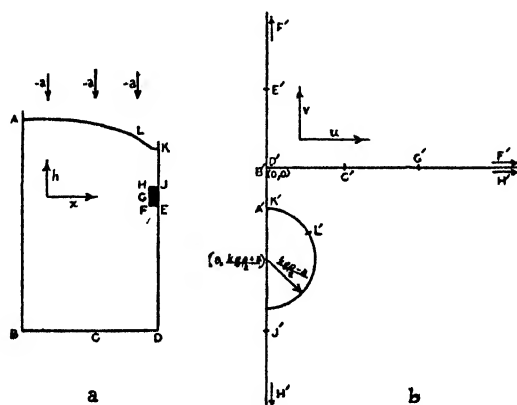


FIG. 10. a. Drainage system element with rectangular drain section; b. Hodograph of the system shown in a.

The remaining boundaries of our problem present no new features, and the hodographs may be drawn in conformity with the rules given by Muskat (7, p. 300 *et seq.*). Thus the hodograph of a system with buried pipe drains, such as figure 10a, is shown in figure 10b, correspondences being appropriately lettered. A drain of rectangular cross section has been chosen because one of any other preassigned shape presents obvious difficulties, the path $E'F'G'H'J'$ in the hodo-

graph having to be replaced in the first and fourth quadrants by a curve which is, in principle, initially unknown. For the open ditch problem of figure 11a the hodograph is given in figure 11b.

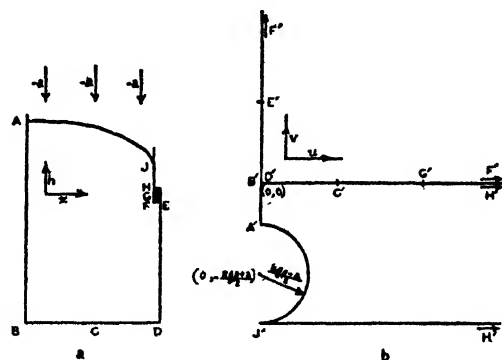


FIG. 11. a. Drainage system element with open ditch, surface of seepage HJ ; b. Hodograph of the system shown in a.

SUMMARY

In a continuance of the study of ground-water movements to drains by means of electrical analogues, it is found (a) that bore holes may cause appreciable perturbation of the water table and stream picture, particularly at the very point of examination; (b) that lowering the level of water in the drains alters the shape of the water table and lowers its height at the midpoint by an approximately equal amount; (c) that an open ditch is a more efficient drain than the same ditch piped and filled in;³ and (d) that neglecting the effect of the capillary fringe causes little error in estimating the position of the water table. The hodograph of a water table at which steady rainfall arrives is shown to be a simple geometrical figure; this is the necessary first step in the analytical solution of such drainage problems.

REFERENCES

- (1) CHILDS, E. C. 1943 The water table, equipotentials, and streamlines in drained land. *Soil Sci.* 56: 317-330.
- (2) CHRISTIANSEN, J. E. 1943 Groundwater studies in relation to drainage. *Agr. Engin.* 24: 339-343.

³ I am indebted to the reviewers of this paper for pointing out that this statement may need qualification in special circumstances. Thus if the open ditch traverses a heavy topsoil, the downcreep may eventually silt and seal the ditch against entry of water, and in areas of irrigation the crust due to evaporation may have a similar effect. A proper bushing or clinkering above the tile drain ensures the maximum efficacy of the open ditch with the convenience, if any, of the filled-in pipe trench, but the bushing should extend to the height of the surface of seepage, and in any event may become ineffective with age. It is to be understood, of course, that the efficiency referred to is purely physical efficiency, which is but one factor, although possibly the basic factor, in overall economic efficiency.

- (3) CHRISTOPHERSON, D. G., AND SOUTHWELL, R. V. 1938 Relaxation methods applied to engineering problems: III. Problems involving two independent variables. *Proc. Roy. Soc. [London]* (A) 168: 317-350.
- (4) FROCHT, M. M., AND LEVEN, M. M. 1941 A rational approach to the numerical solution of Laplace's equation (the four point influence method). *Jour. Appl. Phys.* 12: 596-609.
- (5) HOOGHOUDT, S. B. 1937 Bijdragen tot de kennis van eenige natuurkundige grootheden van den grond: VI. Bepaling van de doorlatendheid, etc. *Bodemkund. Inst. Groningen. Verslag. Landbouwk. Onderzoek.* 43 (13) B: 461-676.
- (6) MUSKAT, M. 1937 *The Flow of Homogeneous Fluids through Porous Media.* McGraw-Hill Book Company, New York.
- (7) SHAW, F. S., AND SOUTHWELL, R. V. 1941 Relaxation methods applied to engineering problems: VII. Problems relating to the percolation of fluids through porous materials. *Proc. Roy. Soc. [London]* (A) 178: 1-17.
- (8) SHORTLEY, G. H., AND WELLER, R. 1938 The numerical solution of Laplace's equation. *Jour. Appl. Phys.* 9: 334-348.
- (9) WYCKOFF, R. D., BOTSET, H. G., AND MUSKAT, M. 1932 Flow of liquids through porous media under the action of gravity. *Physics* 3: 90-113.
- (10) WYCKOFF, R. D., AND REED, D. W. 1935 Electrical conduction models for the solution of water-seepage problems. *Physics* 6: 395-401.

VEGETABLE CROPS IN RELATION TO SOIL FERTILITY: II. VITAMIN C AND NITROGEN FERTILIZERS

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The effects of soil fertility on the nutrient or dietary value of vegetable crops deserve increasing attention in experimental studies. Many investigators are agreed that vegetables are nutritionally superior when produced on soils well supplied with the essential fertility elements, and nutritionally inferior when grown on infertile soils.

With increased plant yields due to the applications of fertilizers, there is usually associated an increase in the total content and concentration of minerals in the plants, but not so frequently of vitamins. If the functions of vitamins in the plant are those of catalytic agents, as described by Schopfer and others (32, pp. 194-197), one would not necessarily expect the concentration of these catalysts to be greater, merely because of an increase in plant size. Rather, a rise in the concentration of the catalyst might indicate a natural plant mechanism to make more effective some element that is deficient in the soil, much as the thyroid enlarges in the human body in an attempt to produce more thyroxine when iodine is deficient, and as parathyroid glands increase their hormone production under calcium deficiencies (6).

This report, which confirms the above hypothesis, gives evidence of an inverse relationship between the concentration of vitamin C in plant tissue and nitrogen supplied as fertilizer, together with the usually positive correlation between this soil treatment and the yields of spinach and Swiss chard. In short, the experiments indicate that the concentration of vitamin C in these leafy green vegetables increases as the fertility of the soil with respect to nitrogen decreases.²

HISTORICAL

Numerous studies have been reported wherein applications of different fertilizers caused increases in the concentration of vitamin C (13, 14, 15, 16, 27, 28), whereas other reports concluded that they do not bring about such increases (19, 23, 31, 34). And now considerable experimental work indicates that the application of fertilizers, particularly nitrogenous ones, may reduce rather than increase the concentration of vitamin C in many vegetable and fruit crops.

Some of the earliest work performed was that of Bracewell, Hoyle, Wallace, and Zilva (4, 5, 35), on the antiscorbutic potency of apples. They concluded that the vitamin was in greater concentration in apples of low nitrogen supply. With all varieties tested, under

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²In this study, concentrations of vitamin C in the leaves and stems and not in the fruit or seed are considered, because vegetative parts portray a truer index of the influence of variable soil fertility than do reproductive organs, which are necessarily more constant in their chemical composition.

the various conditions of nitrogen fertilization, an inverse relationship existed between the nitrogen content of the fruit and the concentration of vitamin C. Similar conclusions were reached by Kessler (20), who reported that fertilizing apple trees with nitrogen depressed the ascorbic acid content of the fruit progressively as the amount of fertilizer was increased. Hahn and Görbing (9) obtained comparable results with spinach.

In several investigations on tomatoes the influence of fertilizers on vitamin content could be noted. Ott (26) reported that tomatoes grown without fertilizer contained more vitamin C than those fertilized with nitrogen, phosphorus, and potassium. Similarly, MacLinn and Fellers (24) found that tomatoes grown under a low nitrogen supply contained 96-136 units of vitamin C, whereas those under high nitrogen had 74-114 units, but the effects of light and nitrogen were not separated in this experiment. More recently very extensive experiments on the tomato have been conducted by Lyon and his co-workers (11, 22). In their nutritional studies, plants grown with sulfate and nitrogen deficiencies resulted in fruit of a higher vitamin C content. The lack of iron produced a significant rise in ascorbic acid.

Again verifying this inverse relationship, Hamdallah (10) found that the vitamin C content of plants which were grown without iron or magnesium was as great as or greater than that of plants fed normally, even though the former were smaller and chlorotic in appearance. In a study of Sudan grass, Wynd (36) reported that the total yield of vitamin C per acre varied inversely as the yield of dry matter and the delivery of nitrogen by the crop. Reder, Ascham, and Eheart (29) studied the effects of fertilizers and environment on the ascorbic acid content of turnip greens and found that potassium and nitrogen produced significant decreases in ascorbic acid. A recent report on grapefruit by workers (18) in Arizona demonstrated an inverse relationship between vitamin C in the juice and nitrogen fertilization.

A careful examination of the literature reveals that environmental factors other than soil nutrient deficiencies may influence the ascorbic acid content. Climatic or other environmental conditions unfavorable for growth frequently result in increased concentrations of vitamin C. Sunny and dry weather, which may reduce the rate of vegetative development, is more conducive to the accumulation of vitamin C than are cloudy and rainy periods (29). Strong light under some conditions has long been recognized as an inhibitor of plant growth, yet light is very influential in increasing the vitamin C content in the plant (12, 30). It is reported (2, 21) that crops grown at high altitudes have an ascorbic acid content sometimes two to three times that of those at lower elevations. Here, again, the high vitamin content is associated with stunted plants grown in an environment unfavorable for maximum vegetative development.

Ascorbic acid is of universal occurrence in growing plants, and it has been demonstrated that there is an enormous increase in its concentration within the germinating seed (25, 30). Bonner and Bonner (3) and Dennison (7) have suggested that it is an essential factor in plant growth. Accordingly, its presence in the plant has been considered something other than merely an accumulation of one of the by-products of metabolism, since it has also been suggested that vitamin C serves as a catalyst in respiration (17, 33). As such, it is allied closely to some of the mineral elements (Fe, Cu, Mn); both are similarly concerned with oxidative enzyme systems. This relationship has been demonstrated, in part, by Elliott and Libet (8), who have shown that an ascorbic acid-iron system exists in the oxidation of phospholipids. Ascorbic acid and a very small amount of iron when used together caused great stimulation of respiration; either one used alone produced some acceleration.

PROCEDURE AND METHODS

Spinach, the Bloomsdale Long Standing variety, was grown under twenty levels of soil fertility in the greenhouse during the winter of 1941-42. Variable amounts of exchangeable ions placed on the clay subsoil of Putnam silt loam offered a means of controlling the fertility of the soil. Since nearly half of the

exchange capacity of this natural clay is taken by hydrogen, various nutrients adsorbed on the clay in exchangeable form may be provided for plants in any desired ratios and quantities, by replacing, more or less completely, the hydrogen by the selected cations and by using the proper amount of the prepared clay in its admixture with sand. The stability of the clay and its naturally high hydrogen content make its use, by simple additions of cations as exchanges for its hydrogen, very convenient.

A series of clay aliquots was prepared by adding calcium acetate to provide 0, 5, 10, 20, and 40 m.e. of calcium. Then from four aliquots of each of these levels of calcium was prepared a nitrogen series by adding 5, 10, 20, and 40 m.e. of nitrogen as ammonium nitrate. This provided, then, twenty different soil treatments giving four levels of nitrogen, each of which had five variable amounts of calcium combined with it as additions to the supply native in the initial clay. To each of these individual treatments were added other nutrients in constant quantities. These additions consisted of 20 m.e. each of potassium and phosphorous and 6 m.e. each of magnesium and sulfate.

The quantity of subsoil clay required to provide the exact exchange capacity for the added nutrients in each treatment was determined beforehand in terms of the known qualities of the clay. This Putnam subsoil material was then mixed under moisture with the particular nutrients and homogeneously blended with pure white quartz sand. Ten replicates of each treatment, or a total of 200 of the mixtures of sand and clay, each in a 1-gallon glazed crock, were prepared. One plant was grown in each. The treatments were randomized on benches and the crocks spaced sufficiently to eliminate light variations. Five of the replicates served for determination of the concentration of vitamin C, while the other five were used for mineral analyses. Entire plants with the exception of roots were utilized.

In the vitamin C determinations, sampling was adjusted such that one plant from each of the twenty treatments was collected at a time, the analyses being completed within 2 to 3 hours after dismantling. This procedure was repeated on consecutive days until the five plants in each treatment were analyzed. In preparation for analyses the material was ground homogeneously in a Waring blender, and vitamin C was determined by modifying slightly the dye reduction method of Bessey and King (1). The vitamin concentration was expressed in milligrams of ascorbic acid per 100 gm. of fresh material.

For the mineral analyses, the plants were collected along with those taken for determination of vitamin C and prepared according to usual methods of harvesting, washing, drying, and preservation. Both fresh and dry weights were recorded. Some determinations were made spectrographically, and others were by regular methods recognized as standard laboratory procedures.

RESULTS

The outstanding features of the crop behavior as influenced by the different fertility levels of the soil were the negative correlation of the concentration of vitamin C with the yields (fresh weights) of the crop; the yields of the spinach

as a more direct function of the amount of applied nitrogen; the more decided response by the crop to the different levels of nitrogen than to those of calcium;

TABLE 1

*Crop yield, and concentration of ascorbic acid and nutrient elements of spinach under variable levels of calcium and nitrogen offered in the soil**

TREAT- MENT NUMBER	APPLIED		ASCORBIC ACID/100 GM.†	YIELD /10 PLANTS	MINERAL ANALYSES OF PLANTS					
	N	Ca			N	Ca	P	K	Mg	Mn
	m.e.	m.e.	mgm.	gm.	per cent	per cent	per cent	per cent	per cent	per cent
1	40	40	70.5 ± 4.7	234.35	6.20	0.71	0.64	8.19	1.25	0.018
5	40	20	84.2 ± 3.6	320.49	6.30	0.69	0.77	7.47	1.03	0.025
9	40	10	88.6 ± 8.5	179.05	6.20	0.64	0.52	7.63	1.05	0.038
13	40	5	82.4 ± 4.8	128.55	6.20	0.79	0.61	7.80	1.07	0.025
17	40	0	120.6 ± 11.1	67.75	6.15	0.63	0.72	7.41	1.06	0.028
Average . . .			89.3 ± 5.0	186.04	6.21	0.69	0.65	7.70	1.09	0.027
2	20	40	95.1 ± 2.8	170.80	4.90	0.80	0.82	8.29	0.99	0.020
6	20	20	108.1 ± 8.1	220.05	5.20	0.64	1.06	8.02	0.85	0.034
10	20	10	87.8 ± 8.1	229.00	5.20	0.64	0.76	6.86	0.91	0.031
14	20	5	81.2 ± 7.0	205.10	5.40	0.59	0.72	7.49	0.83	0.034
18	20	0	124.5 ± 3.8	197.32	5.40	0.50	0.77	7.88	0.92	0.033
Average .			99.4 ± 4.6	204.45	5.22	0.63	0.83	7.71	0.90	0.030
3	10	40	170.2 ± 13.6	85.03	3.20	1.13	1.91	7.92	0.68	0.032
7	10	20	134.1 ± 10.1	108.45	3.10	0.75	1.41	8.39	0.70	0.034
11	10	10	113.4 ± 11.7	138.50	3.75	0.66	1.05	7.39	0.83	0.046
15	10	5	184.4 ± 8.5	153.09	4.95	0.68	0.88	8.07	0.89	0.033
19	10	0	126.5 ± 12.9	99.90	3.85	0.45	1.01	6.92	0.53	0.030
Average . . .			145.7 ± 8.1†	116.99	3.77	0.73	1.25	7.74	0.73	0.035
4	5	40	159.9 ± 8.2	36.49	4.05	1.23	2.61	8.31	0.15	0.016
8	5	20	181.9 ± 18.7	65.37	3.35	0.86	1.96	8.68	0.87	0.022
12	5	10	144.0 ± 19.5	114.90	4.60	0.86	1.08	8.23	0.93	0.034
16	5	5	145.6 ± 10.5	60.10	3.15	0.62	1.31	6.71	0.54	0.049
20	5	0	178.4 ± 11.0	76.70	4.20	0.59	1.26	6.86	0.62	0.040
Average . . .			162.0 ± 7.6†	70.71	3.87	0.83	1.64	7.76	0.62	0.032

* Ascorbic acid per 100 gm. fresh weight, yield in fresh weight per 10 plants, and mineral analyses in percentage of dry weight.

† Each value represents mean concentration with its standard error of five plants or replicates in each treatment.

‡ Mean concentration is greater beyond 1 per cent level of significance than means of treatments receiving 40 or 20 m.e. of nitrogen.

and the relations in concentrations of calcium and phosphorus with that of the vitamin C.

These facts are evident from the summary of the results with spinach as presented in table 1, wherein the treatments for spinach are arranged in groups of

different calcium levels with the same quantity of nitrogen, and then the values averaged for each nitrogen level. Included with the data for concentrations of ascorbic acid and yields of plants are the analyses for six soil fertility elements, viz., nitrogen, calcium, phosphorus, potassium, magnesium, and manganese. It is possible to rearrange these data into groups of four different nitrogen levels, averaged for each constant calcium group, to show the influences of the variable calcium. By this means, its effect regardless of nitrogen can be measured.

That the vitamin concentration in the spinach was increased as the nitrogen supplied in the soil was decreased is evident from the table. The yields suggest the characteristic sigmoid curve of decided increase at certain increments in the levels of offered nitrogen, and then no further increase—possibly decrease—at the higher levels of this applied nutrient. The corresponding yields expressed on a dry weight basis portrayed the same correlations with nitrogen additions and vitamin C concentrations as did the yields in terms of fresh weights, and accordingly are not given.

TABLE 2

Ascorbic acid and calcium in spinach crop as related to yield and nitrogen supplied

Nitrogen applied	m.e.	40	20	10	5
Yield/10 plants	gm.	186.0	204.5	117.0*	70.7
Ascorbic acid/10 plants	mgm.	166.1	203.2	170.5	114.6
Calcium/10 plants	mgm.	1412.0	1416.8	939.4	645.6

Striking correlations of vitamin C with the mineral composition are evident. When the concentrations of ascorbic acid were high in spinach, those of nitrogen and magnesium were low. Neither potassium nor manganese showed any connection with vitamin C. Of added interest is the fact that the concentrations of calcium and phosphorus—usually associated more prominently with anabolic than with respiratory processes—are parallel with those of ascorbic acid.

Some thought may well be given to the fact that the supplies of calcium and phosphorus were constant for each decreasing nitrogen level in the soil, yet these two nutrients moved into the crop in amounts that ran almost parallel with the quantities of vitamin C synthesized. Also of interest is the fact that the total vitamin C accumulation in the crop was less at 40 than at 10 m.e. of applied nitrogen, yet yields were increased by 59 per cent at the higher nutrient level (table 2). Total accumulations of ascorbic acid and calcium suggest that as deficiencies in the soil fertility (nitrogen) produced lower yields of crops, the plants were richer not only in their concentration of this vitamin, but also in calcium and phosphorus. The percentages of total nitrogen, of course, were decidedly lower.

This particular chemical behavior seems reasonable in view of other works dealing with vitamin C and mineral nutrition. Frequently among those reported, there were indications that the greater concentrations and yields of vitamin C occurred, not when optimum conditions of fertility were at hand, but under mineral deficiencies.

It is conceivable that with limitations in the mineral supply, the vitamin C content might increase, since, as previously pointed out, ascorbic acid and some of the minor elements (Fe, Cu, and Mn) "function as coenzymes or fragments of coenzymes" (32) in cellular oxidations. Might the increase in the vitamin concentration of plants serve to offset, in part, deficiencies of essential mineral nutrients, and conversely, an optimum mineral supply in the soil depress the vitamin concentration? Plants may be equipped with more than one mechanism of accomplishing a given reaction or completing an essential process for which, if one means fails or becomes limiting, a substitute may be called in.

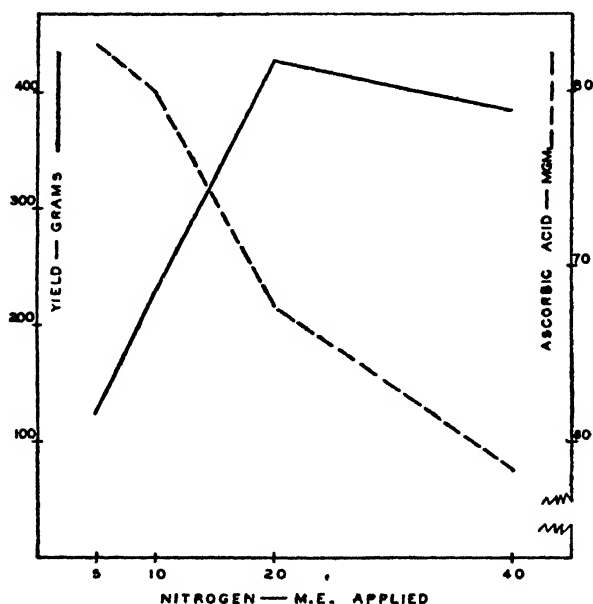


FIG. 1. CONCENTRATIONS OF ASCORBIC ACID AND VEGETATIVE YIELDS OF SWISS CHARD AS RELATED TO NITROGEN ADDITIONS TO THE SOIL

As a confirmation of the results obtained for spinach, Swiss chard was grown during the winter of 1943-44. The experimental conditions were identical to those previously used for spinach. Similar clay subsoil and ratios of calcium and nitrogen were utilized. The summarized results of the influence of different levels of soil nitrogen on the yield of the crop and its ascorbic acid composition, as given in figure 1, portray a repetition of the data already presented for spinach. Again, it was found that with a depression of yields due to deficiencies in soil minerals, the percentage of ascorbic acid in the crop increased; and, conversely, with increased growth and production of vegetative bulk, the concentration of vitamin decreased.

SUMMARY AND CONCLUSIONS

A careful review of the literature indicates that a high rather than a low vitamin C concentration in plants is associated with a reduction in yield due to

nutrient deficiencies, particularly nitrogen. Since certain minerals and ascorbic acid play similar roles as catalysts in plant metabolism, it is suggested that the increase in vitamin C may be a secondary mechanism of the plant to overcome unfavorable conditions of mineral nutrition.

Evidence is presented which indicates that the concentration of vitamin C in leafy green vegetables increases as the fertility of the soil with respect to nitrogen decreases. The following facts were established by the investigation:

There was a decrease in the concentration of ascorbic acid with increasing quantities of nitrogen applied as fertilizer.

A negative correlation was indicated between the yields of the crop and its concentration of ascorbic acid.

There was a decided crop response to nitrogen—as reflected by yields, vitamin C concentration, and mineral content—in some instances quite independent of the calcium levels with which the nitrogen was combined.

The concentrations of calcium and phosphorus within the plant suggest their relation with those for vitamin C.

REFERENCES

- (1) BESSEY, O. A., AND KING, C. G. 1933 The distribution of vitamin C in plant and animal tissues, and its determination. *Jour. Biol. Chem.* 103: 687-698.
- (2) BLAGOVESHCHENSKII, A. V. 1937 The influence of conditions of growth on the vitamin C content of certain plants. *Bul. Biol. Med. Exp.* 3: 189-190.
- (3) BONNER, J., AND BONNER, D. 1938 Ascorbic acid and the growth of plant embryos. *Proc. Natl. Acad. Sci.* 24: 70.
- (4) BRACEWELL, M. F., HOYLE, E., AND ZILVA, S. S. 1930 The antiscorbutic potency of apples. *Biochem. Jour.* 24: 82-90.
- (5) BRACEWELL, M. F., WALLACE, T., AND ZILVA, S. S. 1931 The antiscorbutic potency of apples. III. *Biochem. Jour.* 25: 144-146.
- (6) CAMPBELL, I. L., AND TURNER, C. W. 1942 The relation of the endocrine system to the regulation of calcium metabolism. *Missouri Agr. Exp. Sta. Res. Bul.* 352.
- (7) DENNISON, R. 1940 Growth response of plants to riboflavin and ascorbic acid. *Science.* 92: 17.
- (8) ELLIOTT, K. A. C., AND LIBET, B. 1944 Oxidation of phospholipid catalyzed by iron compounds with ascorbic acid. *Jour. Biol. Chem.* 152: 617-626.
- (9) HAHN, F. V., AND GÖRBLING, J. 1933 Vitaminstudien: VI. Einfluss der Düngung auf den Vitamingehalt von Spinat. *Ztschr. Untersuch. Lebensmitt.* 65: 601-616.
- (10) HAMDALLAH, ABU EL WAFI 1939 Vitamin C—Gehalt Eisen—bzw. Magnesium—frei gezogener Pflanzen. *Protoplasma* 32: 31-43.
- (11) HAMNER, K. C., LYON, C. B., AND HAMNER, C. L. 1942 Effect of mineral nutrition on the ascorbic-acid content of the tomato. *Bot. Gaz.* 103: 586-616.
- (12) HAMNER, K. C., AND PARKS, R. Q. 1944 Effect of light intensity on ascorbic acid content of turnip greens. *Jour. Amer. Soc. Agron.* 36: 269-273.
- (13) HESTER, J. B. 1940 The influence of soil type and fertilization upon yield and composition of tomatoes. *Soil. Sci. Soc. Amer. Proc.* 5: 281-283.
- (14) HESTER, J. B. 1941 Manganese and vitamin C. *Science.* 93: 401.
- (15) IJDO, J. B. H. 1936 The influence of fertilizers on the carotene and vitamin C content of plants. *Biochem. Jour.* 30: 2307-2312.
- (16) ISGUR, B., AND FELLERS, C. R. 1937 A preliminary study of the relationship between vitamin C content and increased growth resulting from fertilizer applications. *Jour. Amer. Soc. Agron.* 29: 890-893.
- (17) JAMES, W. O., AND CRAIG, J. M. 1943 The ascorbic acid system as an agent in barley respiration. *New Phytol.* 42: 28-44.

- (18) JONES, W. F., ET AL. 1944 A note on ascorbic acid: nitrogen relationships in grapefruit. *Science*. 99: 103-104.
- (19) KARIKKA, K. J., DUDGEON, L. T., AND HAUCK, H. M. 1944 Influence of variety, location, fertilizer, and storage on the ascorbic acid content of potatoes grown in New York State. *Jour. Agr. Res.* 68: 49-63.
- (20) KESSLER, W. 1939 Über den Vitamin C—Gehalt deutscher Apfelsorten und seine Abhängigkeit von Herkunft, Lichtgenuss, Düngung, Dichte des Behanges und Lagerung. *Gartenbauwiss.* 13: 619-638.
- (21) KOSTENKO, V. D. 1943 Content of vitamin C in cultivated and wild plants growing in high regions of Pamir. *Compt. Rend.* [Doklady] 38: 42-43.
- (22) LYON, C. B., BEESON, K. C., AND ELLIS, G. H. 1943 Effects of micro-nutrient deficiencies on growth and vitamin content of the tomato. *Bot. Gaz.* 104: 495-514.
- (23) MACK, G. L., TAPLEY, W. T., AND KING, C. G. 1939 Vitamin C in vegetables: X. Snap beans. *Food Res.* 4: 309-316.
- (24) MACLINN, W. A., AND FELLERS, C. R. 1938 Ascorbic acid (vitamin C) in tomatoes and tomato products. *Mass. Agr. Exp. Sta. Bul.* 354.
- (25) NEUBAUER, M. 1939 Das Vitamin C in der Pflanze. *Protoplasma* 33: 345-370.
- (26) OTT, M. 1938 Pflanzenqualität, Volksernährung und Düngung. *Forschungsdienst* 5: 546-552.
- (27) PFAFF, C., AND PFÜTZER, G. 1937 Über den Einfluss der Ernährung auf den Carotin- und Ascorbinsäure-Gehalt verschiedener Gemüse und Futterpflanzen. *Angew. Chem.* 50: 179-184.
- (28) POTTER, M. T., AND OVERHOLSER, E. L. 1933 The vitamin C content of the winesap apple as influenced by fertilizers. *Jour. Agr. Res.* 46: 367-373.
- (29) REDER, R., ASCHAM, L., AND EHEART, M. S. 1943 Effect of fertilizer and environment on the ascorbic acid content of turnip greens. *Jour. Agr. Res.* 66: 375-388.
- (30) REID, M. E. 1938 The effect of light on the accumulation of ascorbic acid in young cowpea plants. *Amer. Jour. Bot.* 25: 701-711.
- (31) SCHEUNERT, A., RESCHKE, J., AND KOHLEMANN, E. 1940 Über den Vitamin C—Gehalt der Kartoffeln: IV. Mitteilung: Über den Einfluss verschiedener Düngung. *Biochem. Ztschr.* 305: 1-3.
- (32) SCHOPFER, W. H. 1943 Plants and Vitamins. *Chronica Botanica Co.*, Waltham, Mass.
- (33) SZENT-GYÖRGYI, A. V. 1939 On Oxidation, Fermentation, Vitamins, Health and Disease. *Williams & Wilkins Co.*, Baltimore.
- (34) WACHHOLDER, K., AND NEHRING, K. 1938 Über den Vitamin C—Gehalt verschiedener Kartoffelsorten und seine Abhängigkeit von Düngung. *Bodenk. u. Pflanzenernähr.* (n.s.) 9-10: 708-724.
- (35) WALLACE, T., AND ZILVA, S. S. 1933 The antiscorbutic potency of apples: VI. *Biochem. Jour.* 27: 693-698.
- (36) WYND, F. L. 1942 Comparison of the efficiency of single applications with repeated top dressings of nitrogenous fertilizers in increasing the yield of dry matter, nitrogen, and vitamin C (ascorbic acid) of Sudan grass. *Plant Physiol.* 17: 645-651.

BOOKS

Adsorption. By C. L. MANTELL. McGraw-Hill Book Company, Inc., New York, 1944. Pp. 386, figs. 149. Price, \$4.50.

This book should be of special interest to those who are concerned with the exchange capacities of soils and related properties. The 18 chapter headings are: the unit operation of adsorption; theories of adsorption; fuller's earth and activated clays; aluminum oxide base materials; bone char and related materials; decolorizing carbons and water-treatment carbon; metal- and medicinal-adsorbent chars; gas-adsorbent carbons; silica gel; magnesia and hydrous oxides; solvent recovery and adsorption from gases; odor removal; gas masks; gas hydrates; dehydration of air and gases; ion exchangers; chromatographic adsorption analysis; and inspection, specifications, and testing of adsorbents. The book has been written from the engineering viewpoint, but that should not impair its usefulness to those who are engaged in scientific research on soils.

Fundamentals of Physics. By HENRY SEMAT. Farrar and Rinehart, Inc., New York, 1945. Pp. 593, figs. 368. Price, \$4.

This is a well-prepared and well-illustrated text dealing with mechanics, heat, electricity and magnetism, wave-motion and sound, and light. It is designed for first-year college students in a five-hour course of which laboratory work constitutes an important part. Most of the material is presented on the level of what might be thought of as the average student, but certain portions of the book are considerably elevated above that plane so that the exceptional student has an opportunity to test himself out in their mastery. It is difficult to conceive of the student who would not be greatly benefited by having learned the essentials of physics as revealed in this text. The author is to be congratulated on having laid the groundwork for an exceptionally good course in this subject.

The Living Soil. Third edition. By E. B. BALFOUR. Faber and Faber Ltd., London, 1944. Pp. 248, plates 13, figs. 9. Price, 12/6.

According to the author, this book concerns health, food, soil, science, and post-war planning. It also concerns legislators, politicians, voters, taxpayers, farmers, gardeners, veterinarians, doctors, sanitary inspectors, school teachers, and priests. Its thesis is that health is to a large degree dependent upon correct soil management. The central theme is: "What's grown with chemicals may look all right, but it ain't got the stay in it." The answer lies in humus, which "confers on plants a power of disease resistance amounting, in some cases, almost to immunity." It naturally follows, therefore, that "the health of the crops grown with it can be transmitted to animals." This leads to a consideration of the means of composting organic wastes, particular stress being laid upon Sir Albert Howard's methods as given in his *Agricultural Testament*.

THE EDITORS.

LEAF ANALYSIS IN ESTIMATING THE POTASSIUM, MAGNESIUM, AND NITROGEN NEEDS OF FRUIT TREES¹

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During the last few years there has been increasing interest in the value of tissue analyses for the diagnosis of nutritional deficiencies of fruit trees, as well as of other plants. In New York leaf analyses have been found helpful in furnishing measures of the needs of fruit trees for potassium, magnesium, and nitrogen fertilization. It is the purpose of this paper to bring together data that indicate the usefulness and some of the limitations of such analyses.

RELATION BETWEEN LEAF ANALYSIS AND NEEDS FOR K, Mg, OR N

Potassium

There is a wide range in percentage (dry weight) of potassium that may be found in samples of leaves from one kind and variety of fruit tree growing under different conditions. Leaf samples taken from 204 New York McIntosh apple orchards in midsummer of 1911 (6) ranged from 0.50 to 2.64 in percentage (dry weight) of potassium. Batjer and Magness (1) found in a large number of Red Delicious apple leaves, sampled similarly in several important fruit areas, a range from 0.70 to 2.73 per cent potassium. Lilleland and Brown (19) found in samples of Elberta peach leaves from 130 California orchards a range from 0.60 to 3.43 per cent potassium.

The leaf scorch symptom of potassium deficiency seems to occur rarely in fruit trees when potassium is above 1 per cent of the dry weight of shoot leaves in midsummer. When the leaf potassium is between 1 and 0.75 per cent of the dry weight of shoot leaves, sampled in midsummer, some potassium deficiency leaf scorch may develop in the latter part of the growing season. When the potassium level of such samples is below 0.75 per cent, leaf scorch develops on the tree more often than not. This has been established for apple and peach trees under greenhouse conditions (15) and is indicated under orchard conditions in field studies with plum, apple, peach, and sour cherry trees (3, 12, 13, 15, 23, 28).

Recovery from serious cases of leaf scorch, when the trees are fertilized with potassium salts, is accompanied by sharp increases in leaf potassium. The magnitude of change in leaf potassium due to soil treatment is indicated in table 1, which summarizes data from three studies (3, 8, 13).

Thus the range, the relation between occurrence of a deficiency symptom and leaf analysis, and the association of increase in leaf potassium with recovery

¹Contribution from the pomology department, Cornell University, Ithaca, N. Y. This paper was presented at the meeting of the Division of Fertilizer Chemistry, American Chemical Society, at New York City, in September, 1944.

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from the deficiency symptom all suggest the usefulness of leaf analysis for potassium as a diagnostic tool.

Magnesium

Although the values are lower than those for leaf potassium, there is a wide range in percentage (dry weight) of magnesium that may be found in leaves from one kind and variety of fruit growing under different conditions. In the study of 204 New York McIntosh apple orchards mentioned previously (6), the magnesium analyses of shoot leaves varied from 0.06 to 0.62 per cent of dry weight. Similar analyses by other investigators for the most part fall within this range (17, 26, 29).

TABLE 1

*Potassium content of leaves, in relation to response of some New York orchards to potassium fertilization**

FRUIT, KIND AND VARIETY	TREATMENT	DATE OF SAMPLING AND OBSERVATION	MEAN LEAF K†	ESTIMATED RE- COVERY FROM SYMPTOMS VISIBLE BEFORE FIRST TREATMENT
			<i>per cent</i>	<i>per cent</i>
McIntosh apple	+ KCl	7/27/42	1.72	100
	Untreated		0.57	0
R. I. Greening apple	+ KCl	8/16/40	1.32	70
	Untreated		0.17	0
Elberta peach	+ KCl	7/25/43	2.11	80
	Untreated		0.72	0
Montmorency cherry	+ KCl	7/25/43	1.90	90
	Untreated		0.45	0
Italian prune	+ KCl	8/15/40	2.20	75
	Untreated		1.13	10

* For details of these studies, see (3, 8, 13).

† Expressed on the dry-weight basis

The leaf blotch symptoms of magnesium deficiency seem to occur rarely in apple trees when magnesium is above 0.25 per cent of the dry weight of shoot leaves taken in midsummer. When the leaf magnesium is between 0.25 and 0.15 per cent, some magnesium-deficiency symptoms may develop in the latter part of the growing season. When the magnesium level of such samples is below 0.15 per cent, leaf blotch seems to develop more often than not. There is considerably less quantitative evidence about these relationships for magnesium than there is in the case of similar relationships for potassium, but the published data of Wallace (29), Kidson, Askew, and Chittenden (17), and Southwick (26), as well as our own (5), indicate such relationships for several apple varieties.

Recovery from serious cases of leaf blotch when the trees are sprayed, injected, or fertilized with magnesium salts is accompanied by considerable increases in leaf magnesium. The relationship between response and leaf analysis is indicated in table 2, which summarizes data from a previously reported study (5).

Thus the range, the relation between occurrence of deficiency symptoms and leaf analyses, and the association of increase in leaf magnesium with recovery from deficiency symptoms all suggest the usefulness of leaf analysis for magnesium as a diagnostic tool.

Nitrogen

Though the range in the total nitrogen (as percentage dry weight of shoot leaves sampled in midsummer) in leaf samples from apple trees growing under different conditions is considerable, it is less than that for potassium or for

TABLE 2

*Magnesium content of apple leaves in July in relation to response to magnesium fertilization**

APPLE VARIETY	TREATMENT	MEAN LEAF Mg†	ESTIMATED RECOVERY FROM SYMPTOMS VISIBLE PRIOR TO FIRST TREATMENT
		<i>per cent</i>	<i>per cent</i>
Bearing Cortland tree	3 Epsom salts sprays	0.26	90
	Untreated	0.13	0
Bearing McIntosh branches	Epsom salts injection	0.22	100‡
	Untreated	0.05	0
Bearing McIntosh tree	Soil applications:		
	3 years Epsom salts	0.17	70
	3 years Epsom salts and lime	0.21	100
	Untreated	0.11	0
Young McIntosh tree	Soil application:		
	1 year Epsom salts	0.19	70
	1 year Epsom salts + KCl	0.19	30
	Untreated	0.07	0

* For details of these experiments, see (5).

† Expressed on a dry-weight basis.

‡ No actual recovery occurred, but the progressive development of the symptom was halted in the year of injection.

magnesium. In a survey made in the summer of 1941, including 78 New York McIntosh apple orchards under commercial management, the total nitrogen in shoot leaves ranged from 1.59 to 2.65 per cent (4). Magness, Batjer, and Regeimbal (20) found in leaf samples taken in October from 105 Rome Beauty apple trees under different nitrogen fertilizer treatments, a range of total nitrogen from 1.34 to 2.03 per cent. Evidence will be presented subsequently to indicate that the lower levels of nitrogen found by Magness and his co-workers were probably due in part to the later date of sampling.

Fruit trees show a number of different kinds of responses to nitrogen fertilization that may be of significance to growers. Heavy nitrogen fertilization of

the McIntosh apple tree, for instance, promotes vegetative growth and maximum yields, but it also retards the development of red surface color of the fruit, promotes abscission of the fruit before it has attained satisfactory maturity, and shortens the storage life of the fruit (4, 7, 24). The problem of the McIntosh producer, thus, is to maintain a balance between nitrogen fertilization heavy enough to approach maximum fruit production and that light enough to permit maximum development of fruit color and quality. The problem is complicated by the fact that a tree is able to store nitrogenous materials in considerable quantity. Measures of the nitrogen reserve in the tree during one growing season

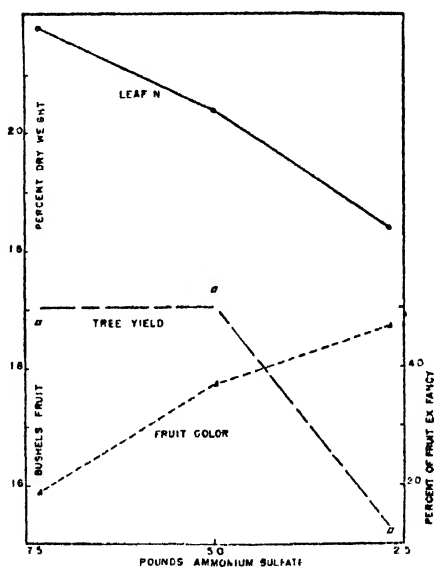


FIG. 1. EFFECTS OF THREE LEVELS OF AMMONIUM SULFATE FERTILIZATION ON LEAF NITROGEN, TREE YIELDS, AND FRUIT COLOR IN A WESTERN NEW YORK MCINTOSH APPLE ORCHARD, 1913

are useful in furnishing a basis for anticipating the nitrogen needs for the next season.

Total nitrogen in shoot leaves of McIntosh apple trees sampled in midsummer seems to be one such measure. Figure 1 shows, for one New York McIntosh apple orchard, the relationship between nitrogen fertilization and leaf nitrogen and the relationships between leaf nitrogen and yield and between leaf nitrogen and average fruit color at harvest time. Our studies to date (4, 7) indicate that McIntosh apple trees having shoot leaves with total nitrogen content in midsummer between 1.85 and 2.00 per cent of dry weight are close to the optimum balance. When such samples contain much more than 2.00 per cent nitrogen, fruit color and quality often are seriously reduced without increase in yield; when they contain less than 1.85 per cent nitrogen, yield may be considerably curtailed although fruit quality is often excellent.

FACTORS INFLUENCING INTERPRETATION OF LEAF ANALYSIS DATA

If one could arrive at satisfactory solutions of possible potassium, magnesium, or nitrogen problems by analysis of leaves sampled any time, anyhow, anywhere, estimation of the need for fertilizers containing these nutrients would be simple indeed. Unfortunately, however, the condition of the root system and conducting tissues of the tree, the possibility of injury to the leaves from toxic sprays or fertilizers, the age of the leaves, the climate, the season, ionic interrelationships, and the kind and variety of fruit, all should be taken into account in the interpretation of leaf analysis data.

TABLE 3

Influences of root, trunk, and leaf injuries on the chemical composition of apple leaves

FRUIT, KIND AND VARIETY	CAUSE OF INJURY OR TREATMENT	TREE SYMPTOMS WHEN SAMPLED	DATE SAMPLED	MEAN LEAF ANALYSIS*		
				K	Mg	N
				<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Northern Spy apple	Soil flooded 9 months	B deficiency	8/29/39	0.58		1.05
	Normal	None		1.65		1.85
McIntosh apple	Spray injury to foliage	Leaf scorch	7/—/39	1.12		
	Normal	None		1.31		
McIntosh apple	Cyanamid injury	Leaf scorch	7/—/39	0.63		
	Normal	None		0.74		
McIntosh apple	Winter injury to sapwood	Leaf scorch and chlorosis	10/15/42†	0.63	0.16	1.46
	Normal	None		0.61	0.22	1.64
Elberta peach	Borer injury to trunk	Leaf rolling	10/14/41†	0.78	0.50	
	Normal	None		0.82	0.59	...

* Expressed on a dry-weight basis.

† Low percentages of potassium due in part to late date of sampling.

Influences of root, trunk, and leaf injuries

Indications of the effects of anaerobic soil conditions, borer injury to the trunks of trees, winter injury to the sapwood of trees, spray injury, and cyanamid injury on the chemical composition of apple leaves are given in table 3, which is summarized from published (16, 23) and unpublished data. The data, though not conclusive, seem to suggest that any conditions resulting in inability of the root system or conducting tissue to function normally, will be likely to reduce the potassium, magnesium, and nitrogen (expressed as percentage dry weight) found in fruit tree leaves. The effect of spray injury to the foliage is apparently also in that direction. Thus, before leaf samples are taken for

chemical analysis, the possibility of these complications should be carefully evaluated.

Influence of age of leaf

The plant material sampled for chemical analysis should reflect the nutrient status of the plant. For grapes (27) and sugar beets (11) the first "mature" leaf has been found best to reflect this condition. For fruit trees, median shoot leaves have been most commonly used (5, 7-10, 13, 14, 19, 20). Apple shoots are fully developed under New York conditions 4 to 6 weeks after full bloom, which normally occurs during the first two weeks in May. Leaf dry weight continues to increase until mid-September. Nitrogen and potassium show a

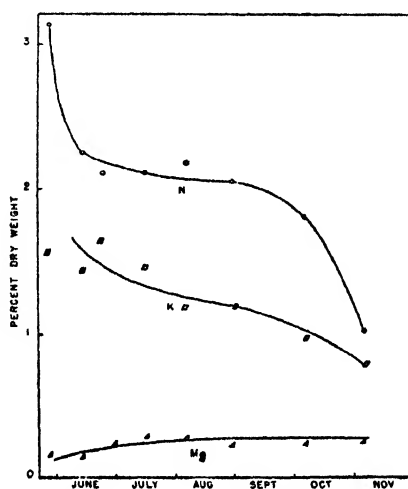


FIG. 2. SEASONAL TRENDS OF NITROGEN, POTASSIUM, AND MAGNESIUM IN LEAF SAMPLES FROM EIGHT MCINTOSH APPLE TREES IN THE CORNELL UNIVERSITY ORCHARD, 1943

progressive decrease, on a dry-weight basis, and magnesium a very slight increase as the season advances, as shown in figure 2. These changes in percentage of potassium, nitrogen, and magnesium are thus associated with increasing age of leaf. Edgerton³ found the percentage of potassium to be greater for leaves from the tip than from the base of shoots, whereas Reuther and Boynton (23) reported lower values for potassium in spur leaves than in median shoot leaves which develop a few weeks later than spur leaves. Some of these data are reproduced in table 4. Thus the time of sampling and position of leaves must be chosen with some care in obtaining samples for leaf analysis. Under New York conditions, leaves sampled from July 15 to September 1 from the center half of shoots have proved to be the most satisfactory for a diagnostic approach to the nutrient status of fruit trees.

³Edgerton, L. J. Influence of variations of hydrogen-ion concentration and of potassium on apple plants grown in artificial media. 1941. [Unpublished doctor's thesis. Copy on file Cornell University, Ithaca, N. Y.]

TABLE 4

Percentages of potassium in leaves from different positions on McIntosh apple shoots and from shoots as compared with spurs

Position of leaves on shoots†	LEAF K, PER CENT*
Terminal	1.74
Central	1.66
Basal	1.48
Shoot leaves‡	1.42
Spur leaves‡	1.26

* Expressed on a dry-weight basis.

† Data from Edgerton (unpublished)

‡ Data from Reuther and Boynton (23).

TABLE 5

*Differences of potassium and magnesium percentages in leaves sampled July, 1941, and July, 1942, from 148 New York McIntosh apple orchards**

	NUMBER OF ORCHARDS	LEAF ANALYSIS†	
		K	Mg
<i>Hudson Valley</i>			
		<i>per cent</i>	<i>per cent</i>
1942	73	1.63	0.19
1941		1.53	0.25
Mean difference		+0.10	-0.06
Standard error		0.019	0.005
<i>Western New York</i>			
1942	59	1.48	0.23
1941		1.22	0.28
Mean difference		+0.26	-0.05
Standard error		0.028	0.013
<i>Champlain Valley</i>			
1942	16	1.24	0.26
1941		1.07	0.29
Mean difference		+0.17	-0.03
Standard error		0.044	0.012
<i>Total survey</i>			
1942	148	1.53	0.22
1941		1.36	0.27
Mean difference		+0.17	-0.05

* For full details see (6). The leaf samples were taken from the same trees in both years. Soil management and fertilization were essentially the same both years on all orchards.

† Expressed on a dry-weight basis.

Influence of season and climate

The potassium and magnesium percentages found in apple leaves may vary from season to season. Table 5 shows the mean differences in analysis of composite median shoot leaf samples taken in midsummer from the same trees under the same soil management conditions in 148 New York McIntosh apple orchards in 1941 and 1942 (6). The percentage of potassium was significantly lower and that of magnesium significantly higher in 1941 than in 1942. These differences may have been due to the fact that rainfall was considerably below normal in 1941 and was normal or above normal in 1942. Potassium-deficiency leaf scorch was more prevalent in 1941 than in 1942 and magnesium-deficiency leaf blotch was more common in 1942 than in 1941. The more frequent appearance of deficiency symptoms correlated with lower potassium and magnesium levels indicates that these seasonal differences in analysis may not interfere with the use of leaf analysis in diagnosis. But the data suggest that unlike seasonal conditions may obscure or exaggerate differences of potassium or magnesium percentage in leaf samples from two areas. For example (table 5), both in 1941 and 1942, the potassium percentage was higher for western New York than for the Champlain Valley, but the 1942 Champlain Valley mean was about the same as the 1941 figure for western New York.

As to nitrogen, there seem to be climatic influences on the response of McIntosh apple trees to a given level that may make rather heavy nitrogen fertilization less detrimental to the development of satisfactory fruit color and quality in one region than in another. For instance, in a Champlain Valley orchard in 1943, McIntosh trees with leaves having 2.16 per cent nitrogen in July produced fruit 84 per cent of which was fancy and 40 per cent of which was extra fancy in color at harvest time, whereas in a western New York orchard, trees with leaves analyzing 2.18 per cent nitrogen had fruit with 62 per cent fancy and 19 per cent extra fancy color at harvest time (7). Better color in the Champlain Valley orchard was probably due to cooler temperatures prevailing there prior to harvest. Preliminary data also indicate that yield of fruit may drop seriously in this Champlain Valley orchard if it is not kept at a higher nitrogen level than is needed in the western New York orchard.

Season and climate should be taken into account when leaf analyses are interpreted.

Interrelationships of ions

Under some conditions potassium fertilization seems to induce or to aggravate magnesium deficiency. This effect of potassium fertilization is accompanied by sharp increases in leaf potassium and decreases in leaf magnesium. Table 6 gives some analyses of leaves from a McIntosh apple orchard in which potassium-induced magnesium deficiency was studied (9). In orchards showing magnesium-deficiency symptoms, even though soil replaceable potassium may be low, and though no potash supplements are used, leaf potassium tends to be abnormally high. It seems likely, then, that high leaf potassium may sometimes be a symptom of magnesium deficiency, and analysis for potassium as well as for

magnesium may be helpful in diagnosis of magnesium deficiency. The opposite relationship (high Mg—low K) seems to exist although to a less marked extent.

The percentages of potassium found in the McIntosh apple leaves may be considerably influenced by their nitrogen levels. Figure 3 presents data from three New York McIntosh orchards under differential nitrogen fertilization (10). In all of the plots there was an inverse relationship between nitrogen and

TABLE 6

*Analysis of leaves from McIntosh apple trees showing magnesium blotch after 5 years' fertilization with potassium and of leaves from paired trees not fertilized with potassium and not showing blotch**

SOIL TREATMENT	LEAF ANALYSIS†	
	K	Mg
	per cent	per cent
+ KCl‡	1.36 \pm 0.052	0.13 \pm 0.009
Check	0.65 \pm 0.048	0.33 \pm 0.020

* For full details of this experiment see (9).

† The leaves were sampled for analysis 8/26/43. The figures are the means and standard errors for samples from nine treated and untreated trees, expressed on a dry-weight basis.

‡ From 2 to 5 pounds of commercial KCl (60 per cent) or K_2SO_4 (48 per cent) was applied annually around the trees each year from 1938 to 1942. No potash was applied in 1943.

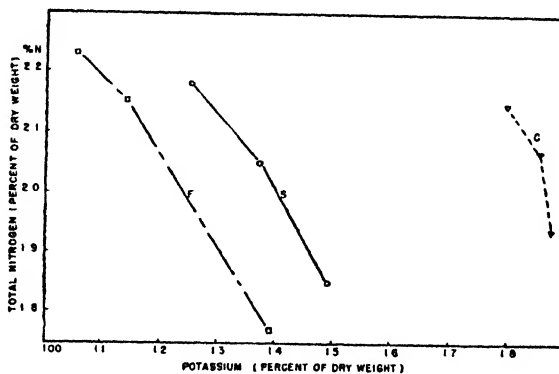


FIG. 3. RELATION BETWEEN PERCENTAGES OF NITROGEN AND POTASSIUM IN LEAF SAMPLES FROM THREE NEW YORK MCINTOSH ORCHARDS, EACH OF WHICH WAS FERTILIZED DIFFERENTIALLY WITH AMMONIUM SULFATE

F = Forrence, S = Shannon, C = Clark. For details of the experiment see (10).

potassium analysis of the leaves. Increased vegetative growth, which varied directly with the nitrogen applications, may account in part for this inverse relationship, but the relationship still existed when the data were expressed on an absolute basis.

In these same orchards a positive relationship existed between the nitrogen and magnesium percentages in the leaf samples. This is shown in figure 4.

The relationship appeared more marked when the data were expressed on an absolute basis.

Undoubtedly other ionic relationships, some of which have been studied with other plant materials [(21, 22, 25) for instance], will be found to have some bearing on the percentages of nitrogen, potassium, or magnesium in fruit tree leaves.

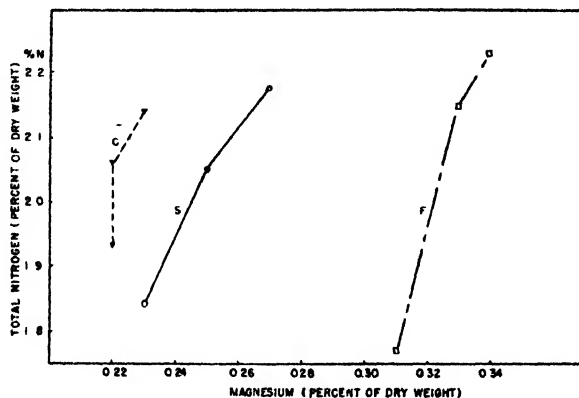


FIG. 4. RELATION BETWEEN PERCENTAGES OF NITROGEN AND MAGNESIUM IN LEAF SAMPLES FROM THREE NEW YORK MCINTOSH APPLE ORCHARDS EACH OF WHICH WAS FERTILIZED DIFFERENTIALLY WITH AMMONIUM SULFATE
F = Forrence, S = Shannon, C = Clark. For details of the experiment see (10).

TABLE 7

*Mean nitrogen, potassium, and magnesium percentages in leaves from adjacent McIntosh apple and Elberta peach trees in seven orchards, July, 1941**

	N	K	Mg
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
McIntosh apple	1.97 \pm 0.06	1.24 \pm 0.17	0.29 \pm 0.05
Elberta peach..	3.54 \pm 0.10	1.67 \pm 0.28	0.55 \pm 0.04

* Expressed on a dry-weight basis.

Influence of kind and variety of fruit

The percentages of nitrogen, potassium, and magnesium normally found in a leaf sample taken in midsummer vary also with kind and variety of fruit. Table 7 presents the means of leaf analyses from seven commercial orchards in which Elberta peach and McIntosh apple trees were growing adjacent to each other. The nitrogen and magnesium levels of the peach leaves are strikingly higher than the levels of those constituents in the apple leaves. There may be some question as to the significance of the higher potassium level of the peach leaf sample. The analyses of Cullinan and Batjer (15) for nitrogen and potassium and those of Lilleland and Brown (18) for potassium also indicate higher percentages of the nutrients in peach leaves than in apple leaves from trees

growing under the same conditions. Leaves from Montmorency cherry and Italian prune trees also seem to have higher percentages of nitrogen, potassium, and magnesium than do leaves from apple trees of similar age and environment.

There may also be differences among varieties of apple in the percentages of nitrogen, potassium, and magnesium normally found in leaves from trees under conditions for optimum productivity. Batjer and Magness (1) have found higher percentages of potassium in the leaves from Delicious apple trees than in leaves from Rome Beauty and York growing under the same conditions. Blake, Nightingale, and Davidson (2) have suggested that the calcium requirement of the varieties Delicious and Stayman is higher than that of McIntosh and Baldwin. It is desirable to fertilize such culinary apple varieties as R. I. Greening more heavily with nitrogen than red dessert varieties like McIntosh. This heavier feeding probably results in higher nitrogen analysis of the leaves of trees under optimum conditions for productivity.

POSSIBILITIES AND LIMITATIONS OF LEAF ANALYSIS IN ESTIMATING K, Mg, AND N

The fact that the percentages of potassium, magnesium, and nitrogen in the dry weight of fruit tree leaves vary with other factors besides the supply of those nutrient elements does not mean that leaf analysis for them is valueless in diagnostic work. It simply means that the other factors should be taken into consideration when the analyses are interpreted. Properly used, such analyses may furnish extremely valuable evidence in support of, or in contradiction to, tentative conclusions based on other data or observations. Lacking a single infallible criterion of needs of fruit trees for these nutrients, the diagnostician will make use of several indexes the limitations of which are fairly well understood. Chemical analysis of leaves can never take the place of careful observations on tree behavior and appearance, on the development of visible leaf or fruit symptoms, and on past climatic and management conditions that might have caused an abnormality under study; but analyses of leaves together with these observations may make possible a positive diagnosis that neither alone would have permitted.

Undoubtedly it will be possible to substitute semiquantitative methods of analysis for the quantitative ones used here to determine potassium and magnesium. Leaf total nitrogen does not have so wide a range as seems desirable. Preliminary studies by Compton and Boynton indicate that leaf chlorophyll determined by a rapid method may be closely related to total nitrogen under many orchard conditions, has a wider range, and may sometimes be used as an index of nitrogen level.

SUMMARY

Leaf analyses for total potassium, magnesium, and nitrogen, expressed on the dry-weight basis, were found under some conditions to indicate the needs of fruit trees for these nutrients. The composition of fruit tree leaves with respect to those three elements was also found to be influenced by the condition

of the root system and conducting tissues of the tree, injuries to the leaves from toxic sprays or fertilizers, the age of the leaves, the climate, the season, ionic interrelationships, and the kind and variety of fruit tree. Data are presented to indicate the possible significance of these factors. It is concluded that chemical analysis of leaves for these constituents cannot take the place of careful observations on tree behavior and appearance, on the development of visible leaf or fruit symptoms, and on past climatic and management conditions; but that chemical analyses of leaves, coupled with these observations, may make possible a positive diagnosis that neither alone would have permitted.

REFERENCES

- (1) BATJER, L. P., AND MAGNESS, J. R. 1939 Potassium content of leaves from commercial apple orchards *Proc. Amer. Soc. Hort. Sci.* 36: 197-201.
- (2) BLAKE, M. A., NIGHTINGALE, G. T., AND DAVIDSON, O. W. 1937 Nutrition of apple trees. N. J. Agr. Exp. Sta. Bul. 626.
- (3) BOYNTON, D., REUTHER, W., AND CAIN, J. C. 1941 Leaf analysis and apparent response to potassium in some prune and apple orchards, preliminary report. *Proc. Amer. Soc. Hort. Sci.* 38: 17-20.
- (4) BOYNTON, D., AND CAIN, J. C. 1942 A survey of the relationships between leaf nitrogen, fruit color, leaf color and per cent of full crop in some New York McIntosh apple orchards, 1941. *Proc. Amer. Soc. Hort. Sci.* 40: 19-22.
- (5) BOYNTON, D., CAIN, J. C., AND VANGELUWE, J. 1943 Incipient magnesium deficiency in some New York Apple Orchards *Proc. Amer. Soc. Hort. Sci.* 42: 95-100.
- (6) BOYNTON, D., CAIN, J. C., AND COMPTON, O. C. 1944 Soil and seasonal influences on the chemical composition of McIntosh apple leaves in New York. *Proc. Amer. Soc. Hort. Sci.* 44: 15-24.
- (7) BOYNTON, D., AND BURRELL, A. B. 1944 Effects of nitrogen fertilizer on leaf nitrogen, fruit color and yield in two New York McIntosh apple orchards, 1942 and 1943. *Proc. Amer. Soc. Hort. Sci.* 44: 25-30.
- (8) BOYNTON, D., 1944 Responses of young Elberta peach and Montmorency cherry trees to potassium fertilization in New York. *Proc. Amer. Soc. Hort. Sci.* 44: 31-33.
- (9) BOYNTON, D., AND BURRELL, A. B. 1944 Potassium-induced magnesium deficiency in the McIntosh apple. *Soil Sci.* 55: 441-454.
- (10) BOYNTON, D., AND COMPTON, O. C. 1944 The influence of differential fertilization with ammonium sulfate on the chemical composition of the McIntosh apple leaves. *Proc. Amer. Soc. Hort. Sci.* 45: 9-17.
- (11) BROWN, R. J. 1943 Sampling sugar beet petioles for measurement of soil fertility. *Soil Sci.* 56: 213-222.
- (12) BURRELL, A. B., AND CAIN, J. C. 1941 A response of apple trees to potash in the Champlain Valley of New York. *Proc. Amer. Soc. Hort. Sci.* 38: 1-7.
- (13) BURRELL, A. B., AND BOYNTON, D. 1943 Response of apple trees to potash in the Champlain Valley: III. *Proc. Amer. Soc. Hort. Sci.* 42: 61-64.
- (14) CHAPMAN, H. D., AND BROWN, S. M. 1943 Potash in relation to citrus nutrition. *Soil Sci.* 55: 87-100.
- (15) CULLINAN, F. P., AND BATJER, L. P. 1943 Nitrogen, phosphorus, and potassium interrelationships in young peach and apple trees. *Soil Sci.* 55: 49-60.
- (16) HEINICKE, A. J., BOYNTON, D., AND REUTHER, W. 1940 Cork experimentally produced on Northern Spy apples. *Proc. Amer. Soc. Hort. Sci.* 37: 47-52.
- (17) KIDSON, E. B., ASKEW, H. O., AND CHITTENDEN, E. 1940 Magnesium deficiency of apples in the Nelson district of New Zealand. *New Zeal. Jour. Sci. and Technol.* 21: 305A 318A.

- (18) LILLELAND, O., AND BROWN, J. G. 1939 The potassium nutrition of fruit trees: II. Leaf analysis. *Proc. Amer. Soc. Hort. Sci.* 36: 91-98.
- (19) LILLELAND, O., AND BROWN, J. G. 1941 The potassium nutrition of fruit trees: III. A survey of the K content of peach leaves from one hundred and thirty orchards in California. *Proc. Amer. Soc. Hort. Sci.* 38: 37-48.
- (20) MAGNESS, J. R., BATJER, L. P., AND REGEIMBAL, L. O. 1940 Correlation of fruit color in apples to nitrogen content of leaves. *Proc. Amer. Soc. Hort. Sci.* 37: 39-42.
- (21) PIERRE, W. H., AND BOWER, C. A. 1943 Potassium absorption by plants as affected by cationic relationships. *Soil Sci.* 55: 23-36.
- (22) REEVE, E., AND SHIVE, J. W. 1944 Potassium-boron and calcium-boron relationships in plant nutrition. *Soil Sci.* 57: 1-11.
- (23) REUTHER, W., AND BOYNTON, D. 1940 Variations in potassium content of the foliage from certain New York orchards. *Proc. Amer. Soc. Hort. Sci.* 37: 32-38.
- (24) SMOCK, R. M., AND BOYNTON, D. 1944 The effects of differential nitrogen treatments in the orchard on the keeping quality of McIntosh apples. *Proc. Amer. Soc. Hort. Sci.* 45: 77-86.
- (25) SOMERS, I. I., AND SHIVE, J. W. 1942 The iron-manganese relation in plant metabolism. *Plant Physiol.* 17: 582-602.
- (26) SOUTHWICK, I. 1943 Magnesium deficiency in Massachusetts apple orchards. *Proc. Amer. Soc. Hort. Sci.* 42: 85-94.
- (27) ULRICH, A. 1943 Plant analysis as a diagnostic procedure. *Soil Sci.* 55: 101-112.
- (28) WALLACE, T. 1931 Chemical investigations relating to potassium deficiency of fruit trees. *Jour. Pomol. and Hort. Sci.* 9: 111-121.
- (29) WALLACE, T. 1940 Chemical investigations relating to magnesium deficiency of fruit trees. *Jour. Pomol. and Hort. Sci.* 18: 145-160.

PRESENT STATUS OF DIAGNOSIS OF MINERAL REQUIREMENTS OF PLANTS BY MEANS OF LEAF ANALYSIS

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The chemical examination of plant tissue as a guide in fertilizer practice has reached an active stage in the research programs of agricultural institutions. The renewal of this search notwithstanding discouragement by those influenced by the dogmas of traditional agronomy has resulted in a marked advance in our knowledge of that phase of the mineral nutrition of plants relating to soil management in general.

INFLUENCE OF CERTAIN OLDER PROCEDURES

The earlier investigations on the analysis of the plant for the purpose of determining the requirements of a given soil for specific fertilizer elements were based on the storage of salts in the mature plant or plant part. Although some workers were able to establish fixed minima for certain crops below which the need for an element was indicated, failures were many. There are a number of reasons why such procedures are unsatisfactory, some of which have been discussed by Hall (28). One disadvantage is the lack of sensitivity inherent in the data of the analysis of a mass of heterogeneous organs each nourished in its own way. The results led to the view still held by many that the composition of plants is not a good index of the requirements of a given soil for a particular fertilizer as indicated by field trials.

THE MODERN APPROACH

The distinction between the older and newer methods of the analysis of the plant as a means of determining the available nutrients in the soil may be summarized in the statement that the earlier methods were concerned with the quantities of mineral nutrients stored in the mature plant, whereas leaf analysis is based on the functioning assimilating leaves as the control laboratories of nutrition.

The emphasis in the modern work is placed upon the internal concentration of nutrients in the leaf, especially upon the changes in levels during different stages of the growth cycle, in relation to response, that is, to growth and development. The data, accordingly, represent an integration of all the factors that have affected the nutrient content up to the time of sampling. There are, nevertheless, many different procedures, treatments of data, and methods of interpretation of results. These are examined in this paper.

The fundamental relationships sought are: first, the relationship between the external concentration of an element and its uptake by the plant; second, the relationship of the internal concentration of each element to growth, at different levels of the others (interaction of factors).

The uptake of an element is not always in direct proportion to the external concentration, a fact which accounts for the difficulties encountered in the methods of traditional agronomy in seeking too closely for a direct relationship between fertilizer applied and yields.

The amount of an element absorbed is modified to different degrees not only by the nature of the other elements, but also by their relative proportions in the external solution. In nutrient culture experiments this interaction can be studied by keeping other environmental factors constant. In this way, as the experiments of Lundegeårdh (46), Shive *et al.* (8, 9), Cullinan and Batjer (20), Gregory (27), and others illustrate, the relationship of uptake of one of the components, nitrogen, phosphorus, potassium, calcium, or magnesium, in the presence of various proportions of the others can be determined. By such means it has been found that whereas in some cases the concentration of these elements rises in proportion to the concentration of the external solution, in other cases ion antagonism and other disturbing factors upset these relations. The bearing of these facts on procedures of diagnosis is referred to later in this paper.

Under the conditions of practical agriculture the problem is more complex. Apart from the impossibility of keeping under control other factors than those studied, solubility and accompanying ion-exchange relationships between root and soil are not analagous to those existing in nutrient cultures. Nevertheless, experiments such as those indicated are invaluable in determining fundamental principles of uptake of nutrients and in pointing out the direction in which research under field conditions should proceed.

SELECTION OF MATERIAL AND SAMPLING TECHNIQUE

Choice of tissue

Apart from the lack of sensitivity, it is not, in general, feasible in field practice to examine the relationship between internal concentration, fertilizers applied, and growth from data obtained by analysis of the entire plant. The testing consequently must be confined to a small portion of the plant in such a manner as not to affect its growth. Various portions of the plant have been used.

In making a choice of possible tissues, one must be guided by such physiological and practical considerations as sensitivity, homogeneity, and accessibility, particularly with respect to the ability to select morphologically homologous tissues. The region where growth occurs, namely, the meristematic material, has been suggested by some, and this possibility was recently examined in the case of sugar cane with respect to nitrogen by Clements (17) and discarded by him because of lack of sensitivity. Moreover, a serious objection to the use of this type of tissue is the obvious one that, except in the case of secondary growths, the plant may be lost. Petioles only are taken by some investigators and parts of the stem or stalk by others.

Most investigators sample the leaf, the synthetic laboratory of the plant. Only in the leaf are the ontogenetic drifts in the major nutrients known to resemble those in the whole plant (3, 58), and only in the leaf have critical investi-

gations, referred to later in this paper, been made, establishing the validity of conclusions from data on composition in relation to fertilizer applied and to growth and development; with the understanding that the term "leaf" as distinguished from leaf blade includes petiole, in other words, the entire leaf.

Comparative nature of all procedures of diagnosis

Whatever portion of the plant is used, the results are of a comparative nature only. They can never be absolute even if the entire plant is taken, because the composition of a particular species is not a fixed entity (66). Rigorous quantitative comparison is possible only between leaves of the same physiological age taken from plants of the same species and variety grown under the same environmental conditions on a relatively uniform soil (66, 67). In the attempt to overcome this limitation, investigators have sought simplification by various means.

The conditions with respect to uniformity of soil are more easily satisfied when the plants are grown in one location than they are in investigations of the survey type, such as orchard surveys over a scattered region. In the latter, comparable conditions should be maintained with respect to aeration even on the same soil type, since anaerobic conditions resulting from poor drainage cause a reduction in the absorption of nutrients; leaf composition then is not correlated with growth (15, 31). There is, moreover, an optimum range, as Loewing's data (45) on mineral absorption from soils subjected to various rates of aeration indicate: excessive aeration is injurious to growth. The general nature of the processes of uptake of nutrients has been discussed by Hoagland (33, 34). The weight of evidence is that uptake of elements is directly related to the metabolic activity of the plant cells associated with aerobic respiration and reflected in CO_2 production. It would appear, therefore, that the relation of uptake to respiratory rates in most cases is an indirect effect.

Sampling procedure

The problem of obtaining morphologically homologous leaves from herbaceous plants presents little difficulty. The most suitable selection is the oldest leaf that will remain healthy and functioning during the period covered by the sampling. Deficiency of nitrogen, phosphoric acid, or potash leads to a more rapid senescence of leaves (67), and is related to the sudden drop in the rate of uptake of nutrients at the initiation of the reproductive phase (27, 40). The difficulty in sampling procedures caused by the senescence before the end of the growth cycle of the leaf of the rank initially chosen can be overcome by the method of relay sampling described elsewhere (67).

The sampling of tree species is relatively more difficult. The sampling of fruit trees has been discussed by Lilleland and Brown (39), Reuther and Boynton (60), Wallace (80), and more recently by Goodhall (26); and that of forest trees, by Mitchell (53). In the former, the median (2, 4, 81) or basal leaves (39, 40, 41) from the current season's branch growth have been used; in older bearing trees preference has been given by some investigators (40, 60) to the spur leaves from lateral growth originating from fruiting spurs, and by others (26, 80) to

leaves from nonfruiting spurs. Basal leaves from the long shoots are usually small; hence, when growth is inadequate the quantity of sample available may be insufficient for analysis by macromethods. The same considerations frequently apply to spur leaves. Unless, therefore, special considerations determine otherwise, the most suitable type of leaf is the median leaf from the long shoots.

For other species, various types of leaf have been used. Working with grapefruit and cacao, Hardy (29) sampled the first hardened shoot leaf. Ulrich (72, 73) customarily takes the most recently "mature" leaf from grape vines, starting from the tip of the cane (shoot), giving as his reason for the choice that the leaf of this rank, being nearer to the growing point, will reflect changes in the nutritional status better than the older tissues. But it may be questioned whether this explanation is sufficiently cogent, because although the critical point at which demand overtakes supply coincides with the appearance of deficiency symptoms in the leaf at emergence, it does not follow that the youngest leaves reflect the nutritional status better than the older ones. Rather does the accumulative evidence indicate that the older leaves reflect the stage of internal starvation before the younger ones, because nutrients are drawn most rapidly from the older leaves when new growth is taking place. Moreover, selection of the most suitable oldest leaf available has the additional advantage of allowing early sampling. Drosdoff (21, 22) sampled blades from the middle of the nonbearing terminals of tung trees, and Chapman (14) restricted sampling of rubber trees to the largest leaf from each of two well-developed whorls high up in the light and on opposite sides of the tree.

With forest trees Mitchell (52) has had satisfactory results by sampling only those leaves exposed to full sunlight from the end of tagged limbs at a convenient height (near the top of the crown) on the south side of each tree, successive samples being composed of leaves taken at random from branches of the marked limbs. From the fact that there is no evidence of lateral transfer of minerals in tree species (1), Mitchell argues that there may be no advantage in attempting to obtain a representative sample of the entire leaf mass of each tree unless soil conditions vary much from one side of the tree to the other.

The number of leaves sampled is immaterial; the main objective is a representative sample. In herbaceous plants the most satisfactory procedure is to sample all plants in a row, omitting only those that deviate from the average of the treatment (67). For tree species there is considerable variation among different workers in the number of leaves sampled from each tree. When samples are taken periodically during the season, one leaf from each of 10 to 15 shoots provides an adequate sample. Some investigators make a composite sample of 5 to 10 trees; but the decision with respect to the validity of compositing must rest upon the uniformity of nutrition. Lilleland and Brown (41) found that the composition of morphologically homologous leaves of peach trees, when taken even from adjacent trees receiving the same fertilizer treatment, differed greatly. This is also our own experience with apple trees grown on nursery stock in the college orchard.

Since diurnal changes in the composition of leaves are relatively small, no great

error is incurred, under most climatic conditions, when sampling is carried out the same day. The early morning is favored by most investigators. The question as to the frequency of sampling during the season has received the attention of many investigators. Obviously, the longer the period of sampling is extended over the growth cycle, the greater is the information obtained with respect to the course of nutrition relative to the fertilizer treatment. Four to five samplings at intervals of two to three weeks are the most satisfactory (67). When, however, only one sampling is required, the question arises as to which portion of the cycle is best. Mitchell (53), from a consideration of the data on leaves of forest trees collected at five periods from May through September, indicates a preference for the period a few weeks before yellowing when the *absolute* amounts of nitrogen, phosphorus, and potassium are at a maximum; but the objectives in investigations on forest trees are not identical with those of other agricultural crops. The former are concerned not only with the relative "feeding power" of different species, but also with the composition of leaves returned to the forest mat. In diagnostic studies on agricultural crops, present evidence suggests that, when only one sampling is to be undertaken, the earlier the samples are taken, the better. Apart from the fact that the earlier the samples are taken, the greater is the opportunity to rectify deficiencies in the particular season, the early part of the cycle is preferable because the rate of uptake of nutrients, especially before flowering, is higher than later, which results, in general, in greater sensitivity. Moreover, the likelihood of the appearance of the phenomenon of "masking" is lessened at the early period. This results from the fact that the decrease in content of the leaf, with respect to the major fertilizer elements, with increasing maturity does not always proceed in a regular manner; an increase in the concentration of a nutrient with maturity occurs if conditions arise such that its supply to the leaf of the rank considered exceeds demand (36, 37, 40, 67). In this connection it should also be kept in mind that nutrients are withdrawn most rapidly from mature leaves when new growth is taking place, and therefore the greatest changes in nutrient concentration take place during the period of most rapid dry-weight increase of the leaves.

In direct contrast with the view that, when only one sampling is carried out, the earlier the samples are taken, the better, is the procedure adopted by Lundegårdh (47) and described later in this paper. His system of leaf diagnosis on cereal crops is based on samples collected at the flowering stage when the vegetative parts of the plant are fully grown but still vigorous.

Influence of fruiting

For woody growths, the influence of fruiting on the composition of the leaf has been examined by many. The most exhaustive of such studies are those of Lagatu and Maume (38) on *Vitis vinifera* grown on 18 differentially fertilized plots in five locations during a period of 5 years. Samples were taken from shoots containing two clusters, one cluster, and none. The conclusion is drawn that, in general, samples should be taken from shoots of the same productivity. These investigators emphasize that, when for any reason this procedure is im-

practicable, samples from shoots of different productivities nevertheless may be used. Their reasoning is that, although systematic differences in composition occurred according to the degree of fruitfulness, the differences with respect to the values for the total nutrition, that is, the percentage of $N + P_2O_5 + K_2O$, as also with respect to the quality of nutrition, that is, the values indicating their relative proportions (or balance), were similar in direction in the plants from all plots. For example, when the quality of nutrition was improved, as indicated by values approaching those of the optimum, this was accompanied in all cases by an increase in the values representing the quantity factor of nutrition. These findings are of importance because of their bearing on the main point of cleavage between the school that uses the element in minimum as the basis for interpreting results without specifically taking into account also their interrelations, and those who find consideration of the latter to be essential.

Our own findings with both 8- and 40-year-old apple trees in the college orchard indicate that leaves from nonfruiting shoots are not always higher in nitrogen, phosphorus, and potassium throughout the entire growth cycle than are leaves of the same age from shoots bearing fruit. The difference is always small and frequently not greater than the analytical error.

PREPARATION OF SAMPLES FOR ANALYSIS

The various methods of tissue preparation in physiological studies with plants have been reviewed by Broyer (10). The method used will depend upon suitability to the objectives sought. The validity of the procedure for the type of investigations in which it is to be used must then be determined by experiment.

Preference is given by most investigators to initial drying of the leaves at a temperature about 70° C. Rapid drying as soon as possible after collection is desirable to avoid decomposition changes. Chapman (14) has found that loss of nitrogen may occur in leaves from rubber trees when dried immediately after sampling at 100° C. even for only 20 minutes. Accordingly, he discards all samples that fail to maintain their green color after the initial drying.

The question arises whether most or all of the mechanical tissues of the leaf should be discarded on the assumption that the composition of the active metabolic regions of the leaf should give the best indication of nutritional status. This idea has influenced the procedure of many. For example, Chapman (14) removes the midrib from the leaves of rubber trees and eliminates, after grinding, all material not passing a 40-mesh sieve; and Mitchell (52), Ulrich (72), Lilleland (39), and also Drosdoff (22), as already mentioned, remove the petioles. The treatment of leaf material by others is more drastic. Thus, Beauchamp (5, 6) eliminates the skeleton tissue by extraction with 95 per cent alcohol. The resulting "crude chlorophyll" is assumed to represent the major part of those mineral elements present in the cell sap of the leaves which are immediately available for the synthetic processes of the foliage. Burkhart and Page (12) extract the leaves with boiling water on the grounds that the relationship to available nutrients in the soil must be sought in the sap of the conducting tissues. Although this procedure removes all the potassium, both sap-soluble and sap-

insoluble forms, the sap-insoluble fractions of the calcium and the magnesium are only partly soluble in hot water (32, 50).

From *a priori* considerations it would appear that the entire leaf should be used when the purpose is to determine the relationship of the mineral nutrition to yields. Moreover, the critical experiments referred to in the next paragraph were based on the use of the entire leaf tissue. High sensitivity, as already pointed out, is desirable but not at the sacrifice of precision as measured by values representing an integration of all the factors that have affected growth.

OBSERVATIONS ON METHOD OF CHEMICAL ANALYSIS

The form of combination of the element

The different procedures to which reference has just been made are related also to the question of the form of combination in which the element is to be determined analytically. The discussion obviously excludes leaf analysis investigations aimed to throw light on the physiological functions of elements such as those of Lindner and Harley (44) in which fractionation procedures may be required. The form favored by most investigators is the *total* amount of nitrogen, phosphorus, potassium, calcium, and magnesium in whatever combination the elements exist. This procedure is in accord with experience with both nutrient culture (27) and field experiments. Among the latter are those of Lagatu and Maume (38) and of Thomas and Mack (68), who established that the composition of leaves of the same metabolic age of plants grown on the same homogeneous medium (soil and climate) receiving different fertilizer treatments reflects these treatments in the sense that whenever a fertilizer element is effective as determined by the response of the plant to that element, that response is always associated with an increase in the *total* amount of that element in the dried foliage. As previously indicated (67) this is not a principle that could be derived from *a priori* considerations. Furthermore, it has also been experimentally established that under the conditions stated, the composition based on the *total* amount present is related to the development of plants receiving the different fertilizers. Hence for each type of development of a particular species there corresponds a definite mode of chemical evolution as measured by the *total* amounts of the respective elements.

These facts, however, do not deny the diagnostic value of the so-called "tissue" tests of a semiquantitative nature for nitrates, inorganic phosphates, and potassium in the conducting tissues as used and interpreted by Carolus (13), Emmert (23), Gilbert (25), Hester (30), Scarseth (63), Thornton (70), and Wolf (82). The experience of the several workers is that the index value for the soluble unassimilated forms of these nutrients will reflect a deficiency before the plant shows starvation symptoms. Indeed, some workers (63) insist that it is important to differentiate between assimilated and unassimilated nutrient elements when the intent is to ascertain the first limiting factor and when, therefore, the sole purpose is to know whether there is an abundance or absence of soluble nutrients in the conducting tissues. The question is as to the adequacy of such methods in the

search for relationships among composition, fertilizer applied, and yield; for yield as a measure of response is the result of a large number of directed and integrated metabolic reactions which cannot be measured in terms solely of the unassimilated nutrients. Moreover, it cannot be assumed from negative results with such tests that a nutrient has been unassimilated, because nitrates, for example, in some species are reduced in the fine roots (54, 64). The evidence is that nitrates are assimilated in the presence of reductase, phosphates, and carbohydrates (55, 56). Furthermore, unless xylem and phloem are separated, these tests will indicate, particularly in stem tissue, downward as well as upward movement of solutes. It may be questioned also whether conclusions with respect to the assimilation of an element can be based on differences shown by such tests when made on fresh, as compared with dried, tissue. For example, because positive tests for potassium have been found in dried tissue, whereas the test is negative on the fresh tissue, it does not follow that potassium is held in some form of an absorptive complex in the living tissue, as Scarseth (63) believes; this phenomenon could result also from a difference in the permeability of the cells by drying.

As a means of analyzing the soil for available nutrients, the quick "tissue" tests are more effective in determining deficiencies than is diagnosis by means of leaf color; because even in cases of extreme deficiency of an element the color commonly associated with the symptom may show considerable change with variations in temperature, light, and moisture, apparently due to toxic accumulation of different elements with differences in environmental conditions (61).

Analytical procedures

Micro, semimicro, and macro methods, employing the procedures of traditional analytical chemistry, as well as colorimetric, spectrographic, and polarographic methods are in use in leaf diagnosis.

It is considered by some that many of the classical procedures in common use are time-consuming and expensive for routine work. For this reason search is being made for more rapid and more economical methods of determining the total amounts of an element in the leaf without sacrifice of precision. A method meeting these requirements is reported by Lindner and Harley (42) for determining nitrogen. The method is based on treatment of the tissue with concentrated H_2SO_4 in such a way as to permit reduction of nitrates by the organic matter and completion of the oxidation of the latter with 30 per cent H_2O_2 followed by nesslerization. With certain modification Cotton¹ has obtained good results with this method in this laboratory. Further advantages are that the solution thus obtained can serve for colorimetric determination of P, K, Ca, and Mg (43).

In the usual Kjeldahl procedure for the determination of nitrogen, precautions invariably are taken to provide for the estimation of nitric-N by the Gunning modification, because although nitrates rarely are present in the green blades (17, 24, 55, 65, 71) their presence may be indicated in the petioles. In the determination of the inorganic constituents, phosphorus, potassium, calcium, and

¹ Cotton, R. H. Leaf analysis: micro-methods for the determination of nitrogen, phosphorus and potassium. 1944. [Unpublished doctoral thesis. Copy on file Pennsylvania State College, State College.]

magnesium, one procedure is to ash a known amount of the dried leaf tissue at temperatures not exceeding 500° C. to avoid loss of potassium and phosphorus. But some investigators, notably Maume (51) and Gilbert (25), adopt the method of wet combustion of the dried tissue with a mixture of concentrated nitric and sulfuric acids, whereas others [Shive *et al.* (9)] digest with aqua regia, and still others [Mitchell (53)], with perchloric acid. Perchloric acid reacts with organic matter with explosive violence, and its use frequently has been discouraged. Piper (59), however, reports that when at least 2 ml. of conc. H_2SO_4 is present in the nitric-perchloric acid digestion mixture there is no danger. The preference for wet combustion methods is based on the alleged loss of phosphorus and potassium when dry-ashing methods are followed; but the experience of most workers is that losses of these components do not occur if the ash is basic and the temperature is controlled.

The cobaltinitrite method for the determination of potassium has nearly displaced the older gravimetric procedure of precipitation as K_2PtCl_6 . The latter method gives more accurate absolute values because the composition of the potassium chloroplatinate precipitate is always constant, whereas that of the sodium potassium cobaltinitrate varies with the conditions of precipitation, which consequently must be carefully standardized. Cotton,¹ of this laboratory, recently developed a colorimetric method for potassium from the dipicrylamine salt, which has given close agreement with the gravimetric determination as K_2PtCl_6 .

For the determination of phosphoric acid the various modifications of the Denigès molybdenum blue method are gradually superseding the alkalimetric method of Pemberton. In the former, errors resulting from interference of arsenic and also of iron have to be guarded against, and in the latter, precautions have to be taken to ensure the constancy of composition of the ammonium phosphomolybdate, which can best be accomplished by precipitation at room temperature, a procedure which also prevents the precipitation of arsenic.

Calcium is generally determined by titration of the calcium oxalate precipitate with potassium permanganate. Microdeterminations for this element based on a turbidimetric method as calcium oxalate are also in use (43). The method of precipitation of magnesium as magnesium ammonium phosphate is being superseded by precipitation as organic complexes. Both 8-hydroxyquinoline and 1:2:4-aminonaphtholsulfonic acid are in use. Colorimetric methods with titan yellow also have been developed (43).

It is highly desirable to be able to determine all the elements required on one portion only of the ashed sample. Wet-ashing methods such as those adopted by Lindner (42) and Parks *et al.* (57) have this advantage. The latter are able to determine twelve elements, Na, K, P, Ca, Mg, S, Fe, Zn, Cu, Mn, Mo, and Co, in the nitric-perchloric acid digestion from a 5-gm. sample.

TREATMENT OF ANALYTICAL DATA

The unit of measurement

As a matter of convenience and uniformity, better agreement with respect to the units in which the results are expressed is desirable. In the case of the fertilizer elements, usage is about equally divided between expressing the composi-

tion in terms of the elements N, P, and K and in terms of the international units N, P_2O_5 , and K_2O . Both Mitchell (53) and Lundegårdh (47) object to the method of expressing the results as oxides, on the grounds that oxides do not occur as such in plant tissue. This, of course, is true; but it is axiomatic in scientific writing that once the results are obtained the data may be used in any way the investigator sees fit in order to bring out clearly the relationships sought. The fact that results are expressed as N, P_2O_5 , and K_2O does not carry the implication that these components are present in the leaf in this form. But since these are the international units used in practical agriculture and the arts dependent upon it, orientation between the laboratory results and practice (fertilizer applied) is easy. The argument of the objectors, moreover, leads to difficulty in the case of nitrogen. If the content of nitrogen in the leaf is to be expressed in ionic form, how is it to be symbolized? Furthermore, why should phosphorus be expressed as P rather than as PO_4 or HPO_4 or H_2PO_4 , all forms that can be found in the literature pertaining to plant nutrition?

The base of reference

Nor is there agreement among workers as to the basis on which results are to be expressed in terms of leaf material. Although the general usage is to express nitrogen in terms of percentage of the dried foliage, some, for example Wallace (77), express the data for this element in terms of fresh weight of leaves; and Hardy (29) and some others, in terms of the percentage of nitrogen in the ash, on the grounds that although the ash cannot contain nitrogen, nutrient ratios are used as entities in the comparison. In the case of phosphoric acid and potash (and also lime and magnesia) usage is about equally divided between expression in terms of percentages of dried foliage and as percentages in the ash. Inasmuch as growth and development are controlled by the concentration of minerals in the leaf, the logical procedure would appear to be to express results in terms of percentages in the moisture-free foliage and thus to ensure a uniform basis for comparison.

INTERPRETATION OF RESULTS

Two main schools of thought

The problem of interpretation is necessarily closely linked with the means employed to ascertain the relationship of composition, fertilizer applied, and growth and development. Two main schools exist with respect to the procedure best adapted to bring out these interrelationships. The one uses as criteria the selection of minimum values or ranges of each nutrient below which experience has indicated the existence of a deficiency of the particular nutrient element. The other school of investigators also makes use of a quantity factor of nutrition in interpretation and, in addition, evaluates the influence of interference factors by taking into consideration the interrelationships of the nutrients under examination.

Practical application of the principle of minimum ranges

The possibility of using minimum values of an inorganic nutrient as a basis for determining deficiencies has been recognized for many decades by workers with nutrient culture media. In this manner it was found that growth ceases when the concentration of any of a number of elements (N, P, K, Ca, and Mg and probably Mn, Fe, Cu, and B) in the leaves falls below a certain minimum, different for different species and types of growth.

More recently attention has been directed by Macy (48) to the relationship between the percentage of a particular nutrient in the plant and growth. This investigator has brought together evidence from a number of sources indicating the existence of breaks in the curves relating the percentages of an element in the plant with increment in yield. These breaks, according to Macy's analyses, occur at what is designated the threshold "optimum" and "minimum," luxury consumption occurring above the former (the critical value) and poverty adjustment above the latter (the minimum value). From these findings, the deduction is drawn that the sufficiency of a nutrient is a function of its percentage content in the plant.

Minimum values below which a deficiency of a particular element is assumed to exist have been determined by means of leaf analysis and applied in orchard surveys, more especially with respect to the status of potassium in the plant. Thus, Batjer and Magness (4) conclude from a survey of widely separated fruit sections of the United States, that the potassium content of leaves from apple trees in late July is a good index of the available supply of this element when care is taken to select trees of comparable variety and age and grown under comparable soil, fertilizer, and general culture conditions.

Similarly, Cullinan *et al.* (19, 20), Reuther and Boynton (60), and Lilleland and Brown (39) have related the degree of scorch in peach, apple, and prune trees respectively to a low content of potassium in the leaves. As preliminary guides, the workers at the U. S. Plant Industry Station at Beltsville (4, 19) have proposed minimum values of 1.0 and 1.5 per cent in the moisture-free foliage of apple (depending on the variety) and 1.5 per cent in that of peach trees. Reuther and Boynton (60) have found that Batjer and Magness' minimum values of 1.2 per cent K_2O for York and Jonathan apply approximately also to McIntosh trees. They suggest that a range of 0.9 to 1.2 per cent K_2O is intermediate between definite deficiency and adequate supply, with the qualification that this range may be displaced up or down according to the time of the season in which samples are taken. Chapman and Brown (15) have tentatively set a minimum value of 0.25 per cent K_2O for the spring cycle from fruit-bearing branches of orange and lemon trees.

In connection with biennial bearing of fruit trees, Lilleland and Brown (39) observed that minimum values for potassium in the leaf vary with the biennial habit. They find that a bearing tree which exhibits a high level of potassium one season may be at a constantly low level during the following year.

Other members of the California group of investigators have made use of minimum values in a more specific manner by searching for a relationship between the content of a particular element in the tissue and yields, as in Ulrich's (72, 73, 74) field experiments with grapes. This investigator has reported that, in years of sufficient rainfall, yields of fruit were related to the potassium content of the petioles.

Similarly, Chapman (14) found that growth was always correlated with the content in the leaf of the deficient element—leaf nitrogen having the highest correlation with yield. The validity of his procedure was based on experiments in which it was found that in each mature whorl of leaves, the relations between nitrogen in the dried foliage, phosphorus and potassium in the leaf ash, and the fresh weight were logarithmic; the leaf samples were taken in succession from top to bottom of each whorl. Inasmuch as the findings are in accordance with Liebig's law, Chapman concludes that in the range of concentration in these experiments, balance within the plant is of no importance as distinct from the reactions proceeding in the soil outside. But the existence of differences in the mobility of elements alone, even if no other factors were involved, would, as indeed Chapman realized, negate generalizations of this conclusion. Consider, as a simple case, the relations between K and Ca. Even if equal molar concentrations existed in the external solution, the higher mobility of K would change the balance within the plant as growth proceeds.

It is of interest to note that Chapman's experiments were conducted on half a dozen soil types that had been subjected to varying degrees of cultivation and erosion and upon which soil analysis had previously failed as a measure of nutrient requirements.

Critical values or ranges used in the sense of an index value of the sufficiency of an element also are applied in certain instances of malnutrition of unknown origin. The causal factor is sought by analyzing the leaf for a number of suspected limiting elements, and comparing the levels of each element separately with that of normal standards grown under the same soil and climatic conditions. In this way Roach (62) found that the differences in composition of leaves of the same type and age from fruit trees of a particular species and variety growing under widely different conditions are small in comparison with the differences obtained between healthy and unhealthy leaves from trees growing on the same plantation. Roach investigated the composition with respect to the elements Na, K, Ca, Mg, and Fe, and Mn; his conclusions, as he points out, are restricted to those elements, and Batjer and Magness (4) found that the percentage of potash differed little in morphologically homologous leaves from apple trees of the same species, variety, and age from widely separated districts. These findings suggest that the mineral composition of healthy leaves of the same type and age of a particular species and variety tend toward a common standard to which the composition of unhealthy leaves may be referred. In this connection it should be remembered that in tree species, particularly in older specimens, growth appears to be but slowly affected by changes in nutrition until relatively great deficiencies or excesses occur. Other instances in which deficiencies have been discovered by comparison of the levels of a number of suspected elements with normal standards

are the findings of Fudge (24) that magnesium deficiency was the cause of "bronzing" of leaves in seedless varieties of grapefruit, the severity of which was related to the percentage of Mg in the dried foliage and to the reduction in yield of fruit.

A similar procedure was adopted by Drosdoff (21, 22) in the investigations of the malnutrition of tung trees. Also the effects of deficiencies of each of the major elements as well as of iron and sulfur have been examined in woody plants by Wallace (75-78). Wallace used as a means of diagnosis the comparison of the levels of nitrogen, phosphorus, potassium, calcium, and magnesium in the leaves from terminal shoots of malnourished trees with those of adequately nourished trees, but he also noted the effect of one element on another by comparison of their ratios. For example, he found that a deficiency of potassium was associated with relatively high values for Ca, Mg, and P in relation to K.

In the category of investigations in which emphasis is laid on the concentration in the leaf with respect to a particular element, may be placed also the spectrographic studies of Brunstetter, Myers, *et al.* (11, 49) and also those of Roach (62). These investigations are of the nature of surveys to ascertain the mineral composition of plants with respect not only to the major elements but also to the micronutrients such as Al, Fe, Cu, Mn, B, Na, Mo, and Co. The American investigators (11, 49) after examining the composition of different tissues of many varieties of American grapes have concluded that the composition of young leaves is a good index of nutritional conditions with respect to soil, climatic, and cultural differences.

Reference already has been made to the work of the English investigators (62). When spectrographic analysis suggests deficiencies of one or more micronutrients, Roach confirms the findings by applying his leaf injection method. He has found that either the spectrochemical or the injection method is valuable by itself but that a combination of the two is an immense improvement.

The principle of critical values or levels is used also in the interpretation of results of workers using the so-called quick plant-tissue tests (13, 25, 30, 63, 82).

Interactions of a metabolic nature

In the investigations on leaf analysis just described, the method of evaluation is based on the principle of minimum values or ranges, each nutrient element being looked upon as an entity in relation to response. If a particular element is present in quantity considerably above the minimum, then the assumption made is that growth is limited for the time being by some other factor. In this way the concept of limiting factors comes into play, requiring a knowledge, in procedures of leaf diagnosis, of the manner in which the nutrient factors have cooperated. Although the bearing of the relationships of the nutrient elements to one another in the interpretation of results is recognized by most of the workers referred to, such relationships are not specifically considered. These interactions or interferences affect growth both without and within the plant, but interpretations of leaf analysis need obviously be directly concerned only with interactions of a metabolic nature.

In this connection the experiments of Gregory (27) are of interest. In nutrient

cultures with barley it was found that when nitrogen is lacking, yield of grain is proportional to the nitrogen absorbed, according to Liebig's law of the minimum, and that when potassium is deficient the curve of potassium absorbed against yield is of the Mitscherlich type. This falling off in yield is shown by Gregory to be an expression of an interaction effect between the nutrient in minimum and that in excess, the law of the minimum holding only when nutrients are in physiological balance. The Mitscherlich curve, therefore, expresses an interaction effect between the nutrient in minimum and that in excess.

So too, Chapman's (14) experiences indicate that within one range of composition the absolute quantities of the nutrients and not their ratios are important; whereas within another range, the ratios may be the dominant factor. Thus, results of both types may be obtained according to the degree of nutritional deficiency.

Consequently, the existence of differences in the effect factor as determined by the internal concentrations of an element at different levels of the others indicates that, in general, the distinction is to be taken into consideration in the procedure and interpretation of leaf analysis. Richards (61) has indicated how complex are these interactions. Nevertheless, it has been possible in practical agriculture to relate data on the ratios between the major nutrient elements in the leaf together with a consideration of the amounts of each present to growth response, without attempting to elucidate the mechanisms involved.

Methods of examining interrelationships

Use of ratios. The examination of ratios between the elements in the leaf has been well established as a diagnostic procedure. For example, Wallace (77) and others cited by him (79) have found that the ratio of potassium to calcium (K/Ca) serves to distinguish between different kinds of chlorosis due to potassium deficiency and to iron deficiency respectively. In the latter type this ratio is greatly increased.

The investigations of Hardy *et al.* (29) on cacao and grapefruit trees may be cited also to exemplify the value of considering the ratios between the elements as a means of determining the relationship between leaf composition and yields. The ratios N/P_2O_5 , N/K_2O , K_2O/P_2O_5 , CaO/K_2O , and CaO/MgO were examined in leaves from trees grown in Latin-square arrangement. Highly significant positive correlations with yield were obtained for certain ratios. The investigators conclude "increased yields are evidently associated with increased potash content of the leaf and decreased nitrogen and phosphate contents, but the best indices of yield are the leaf nutrient ratios, particularly a low N/K_2O ratio, a high K_2O/P_2O_5 ratio, and a high N/P_2O_5 ratio." Two standards of comparison were equally effective; the one selected from "ideal" trees of known high-yielding capacity and good reputation; the other, from trees giving the highest yields and growth rates in fertilizer plots comprising a suitably designed field experiment.

In field plot experiments with sugar cane using fertilizer mixtures containing fourteen different ratios of N, P_2O_5 , and K_2O , Beauchamp (5) found that the

$\frac{\text{K}_2\text{O}}{\text{N}+\text{P}_2\text{O}_5}$ ratio in the leaf served as the best index of yield of cane. This investigator sampled the sixth leaf from the base $3\frac{1}{2}$ months after planting.

Lundegårdh's system of leaf analysis (47) also may be considered here. Formerly, this physiologist suggested the necessity of using not only the plant but also the surface and subsoil for an adequate diagnosis of fertilizer requirements (46); hence the origin of the somewhat ambiguous expression "triple analysis" which is still retained to represent his recently reported "foliar diagnosis" procedure. The practical value of leaf analysis as a guide to soil fertility was tested by Lundegårdh in 800 field experiments with cereal crops in different parts of Sweden. As pointed out earlier in this paper, samples of leaves were collected at the flowering stage. It was found that the curve obtained by plotting leaf K against increment in yield from potassium fertilizers was approximately hyperbolic. Curves of the same type were obtained for leaf N and leaf P when plotted against increments in yields from nitrogen and phosphate fertilizers respectively. That is, the increase in yield obtained by addition of a fertilizer was an inverse function of the nutrient content of the dried foliage.

Lundegårdh derives an expression that represents the interaction of the factors.

The equation is of the type $y \cdot a = \frac{b}{x^c}$, where a , b , c are constants representing the interaction (interference), and y the increment in yield due to the addition of the fertilizer x . The specific form of the equation is $y \cdot A = \frac{b_1}{x_1^{c_1}} \cdot \frac{b_2}{x_2^{c_2}} \cdot \frac{b_3}{x_3^{c_3}} \cdot C_s$, where y is the increase in yield; A is a constant representing the individual values a_1 , a_2 , and a_3 ; x_1 , x_2 , and x_3 are the percentages of K, P, and N respectively in the leaf; and C_s is a correction constant which brings the values of b_1 , b_2 , and b_3 into agreement with the entire scale of yield increments.

Lundegårdh now considers that soil analysis is necessary only for the solution of special problems, such as physiological disorders due to lack of Mn, Ca, or B or for the estimation of the lime status.

Application of concepts of quantity and quality. It would appear to be a logical deduction from the facts recorded that the most promising approach to the problem of the use of leaf composition as a guide in fertilizer practice is to ascertain how a fertilizer intervenes in nutrition to affect the quantitative and qualitative relations of the elements as determined by the changes in either or both simultaneously during the growth cycle. This conception forms the basis of the procedures adopted by Lagatu (35, 36, 37) and the writer (67).

The composition data are broken up into the quantity factor (the sum of the components) and the quality factor (the ratios between the components). The principal point of departure from the methods of other workers (*e.g.*, Hardy, Wallace, and others) is the consolidation of the latter into a unit, which can be readily depicted by means of a point representing the ratios of all three components. This unit, the *NPK-unit* (or *CaMgK-unit* when the bases are considered) is obtained by converting percentage values into milligram equivalents

and then finding the proportion which each bears to the milligram equivalent total. The values so obtained are multiplied by 100 to avoid fractional values (67). These values can then be represented in trilinear coordinates.

Objection has been raised by Gast,² on the basis of inutility, to the procedure of converting percentage values to milligram equivalent values because the value for a particular component at the moment of sampling is multiplied by a constant factor. But the reason for expressing the quality factor in milligram equivalents is that inasmuch as the *NPK-unit* values are, in effect, equilibrium values between the components considered at the moment of sampling, expression in terms of equivalents is the only valid method of expressing chemical reactions. On the other hand, it would be fastidious to express the *quantity* factor in equivalents, for in this case only the quantities of the elements in the leaf are under consideration.

Interpretation of results is made on the basis that a fertilizer intervenes in the nutrition of a plant so as to affect a change either in the *quantity* factor or in the *quality* factor or in both simultaneously. These values are designated "foliar diagnosis values" or the "foliar diagnosis indexes."

This method of interpreting data is being followed by other workers. Thus, Beauchamp (7) in a field plot experiment with potatoes using eight different ratios of a complete fertilizer found a high correlation between yields of tubers from the different plots and the corresponding values expressing the intensity of nutrition and the composition of the *NPK-units*. Also Clements (16) has compared the intensity of nutrition and the composition of the *NPK-units* of the elongating cane leaves from field-grown sugar cane and of those from nutrient cultures. The phase of Clements' work of particular interest here is the result obtained (in nutrient cultures) on the effect of the omission of both micronutrient and macronutrient elements on the "foliar diagnosis indexes." For example boron deficiency doubled the intensity value compared with that of the "complete" solution and was reflected in an increase of K_2O in the *NPK-unit* made at the expense of the N and P_2O_5 . A deficiency of iron increased the intensity of nutrition and was reflected in an increase of P_2O_5 in the *NPK-unit* made at the expense of the N without affecting the K_2O .

The findings of Clements lend support to our hypothesis (69) that a deficiency of any of the micronutrient elements will influence the "foliar diagnosis indexes" with respect to nitrogen, phosphorus, and potassium, to produce abnormalities in the values for the indexes characteristic of the deficient element. The influence of the bases lime and magnesia on the displacement of the N-P-K equilibrium in field experiments has been determined [(69) and references therein]. Although much further work is required to elucidate the effects of deficiencies of the micronutrient elements on the uptake of the major elements, the criticism that other elements are ignored cannot be made against procedures of leaf analysis that report data from fertilizer experiments for nitrogen, phosphorus, and potassium only. When results for the major fertilizer elements only are reported, the implication is that other nutrients are present in available form in the soil in

² Gast, P. E. Private Communication. 1941.

sufficient amounts and in proper balance in the plant and that, consequently, differences in yields are related to foliar diagnosis values with respect to the fertilizer elements. This interpretation is particularly applicable to leaf analysis data on plants grown on such soils as the Hagerstown series, which when limed respond, in general, only to nitrogen, phosphorus, and potassium.

The question whether or not the sum of the concentrations (the intensity index) is of less direct value than the individual concentrations has no significance in the procedure outlined, inasmuch as the concentrations of the individual nutrients are determined periodically during the growth cycle. The relationship of each to response can, therefore, be examined.

Integration of growth to meteorological conditions

In the systems of diagnosis considered, the integration of the mode of nutrition to weather in a particular year (or season) is carried out by conducting experiments on the same location over a sufficient number of years to determine the limits of the physiological changes in the nutrition of the particular crop (69). Clements and Kubota (18) recently reported the results of investigations on sugar cane in which integration of limiting soil factors to the weather ("the available atmospheric energy") is carried out by following the changes in a "primary index" as the plants grow, and is called the "crop log." This index, which is the total sugar in the cane sheaths or blades, has been found by these investigators to be a measure of the balance between photosynthetic production on the one hand and utilization or growth on the other, as related to the environmental condition. The most important factors listed as affecting this index are sunlight, air temperature, water, growth rate, and the nutrient elements commonly deficient. They found that as the intensity of the external factors of sunlight and temperature increased, the primary index increased, and as the intensity of the internal factors of growth and water increased, the primary index dropped. From this behavior these workers consider this index to be a valuable guide in fertilization, irrigation, and crop management in general. Clements concludes that "when the primary index indicates unfavorable trends the specific secondary index (water, nitrogen, phosphorus, potassium, calcium, etc.) reveals the cause. In this way the plant itself is informing the grower of its hazards and when such deterring factors are possible of correction the grower may come close to realizing maximum returns from the energy available." The use of the index in seven field experiments in different locations is described in detail.

SUMMARY AND CONCLUSIONS

Earlier views to the effect that the composition of plants cannot be used as an index of fertilizer requirements are shown to be untenable. The experimental evidence is overwhelming that the transformations which take place in the leaf constitute determinative processes that regulate growth and development; the leaf, therefore may serve as an index tissue in the integration of all factors that influence the availability of soil nutrients and their uptake by the plant.

It is apparent from this review that although the fundamental principles in-

volved in the use of the leaf as a means of diagnosis govern its use as a tool in diagnosis, the use to which the principles are applied does not appear to be always adequate, and when adequate, procedures differ. From at least the standpoint of comparative results of a particular investigator, some of these differences may not be consequential. To such belong, possibly, sampling technique as well as the methods of analysis. But other differences in procedures among workers are worthy of attention, particularly the treatment to which the leaf is subjected before analysis and the manner in which the results are used.

The use of extracting agents such as boiling water or alcohol, as well as the use of only the softer green tissues after grinding, is based on the view that the skeleton or mechanical leaf tissue should not be included, either because only the mineral elements of the conducting tissues have any relation to growth and development, or because selected tissues show greater sensitivity. But the fundamental physiological experimental basis in support of these assumptions is lacking. Since growth and development represent an integration of metabolic reactions within the leaf, it is experimentally sound to include elaborated and unelaborated material when the purpose is to relate nutrition to yields. It is recognized, nevertheless, that in certain types of investigations such as those concerned with diagnosis of the nutritional status of crops as an index of the amounts of available nutrients in the soil, tests for unassimilated nutrients (nitrates), inorganic phosphates, and potassium have proved to be a valuable diagnostic tool. In this category are the so-called rapid "tissue" tests.

Relative to nomenclature, it is apparent that the practical advantages of expressing the results for the fertilizer elements in terms of the international units, N, P_2O_5 , and K_2O , outweigh any possible disadvantages due to conflict as to the implication of the form in which these elements exist in the leaf.

The few workers who have expressed results in terms of the ash of the leaves have deemed this procedure desirable when nutrient ratios were used as entities for comparison. Since growth is governed by the internal concentrations of nutrients, the logical method of expressing results would appear to be on the uniform basis of percentages in the moisture-free foliage, and, in fact, it is upon this basis that the fundamental experimental work of exploring the relationships has been conducted.

The use of minimum or limiting values of each nutrient has been found to be of service in diagnosis, particularly in detecting deficiencies resulting in diseases of a physiological nature; nevertheless, the weight of evidence points to the inadequacy of this method of approach as a basis of ascertaining relationships of composition to yields.

In field fertilizer plot experiments with the commonly deficient elements nitrogen, phosphorus, and potassium, the most effective procedure is one that will give not only a quantitative measure of these nutrients present in the leaf at the moment of sampling, but in addition, an index of the qualitative relations resulting from their interactions. This method of approach has been used by many investigators, but without a uniform methodology. The simplest practi-

cal manner of accomplishing this is by a consideration of the effect of a fertilizer in modifying the quantity and quality factors of nutrition. The latter is expressed by the ratios between the fertilizer elements in the leaf determined at different periods during the growth cycle and is best represented, visually, by means of trilinear coordinate diagrams.

The effects of deficiencies of the micronutrient elements are noted, but additional information is required before generalizations can be made with respect to their interactions with the fertilizer elements.

REFERENCES

- (1) AUCHTER, E. C. 1923 Is there normally a cross transfer of foods, water and mineral constituents in woody plants? *Md. Agr. Exp. Sta. Bul.* 257.
- (2) BAKER, C. E. 1941 The effect of different methods of soil management upon the potassium content of apple and peach leaves. *Proc. Amer. Soc. Hort. Sci.* 39: 33-37.
- (3) BALLARD, L. A. T., AND PETRIE, A. H. K. 1927 Physiological ontogeny in plants and its relation to nutrition. The effect of nitrogen supply on the growth of the plant and its parts. *Aust Jour Exp. Biol. and Med Sci.* 15: 385-404.
- (4) BATJER, I. P., AND MAGNESS, J. R. 1938 Potassium content of leaves from commercial orchards. *Proc. Amer. Soc. Hort. Sci.* 36: 197-201.
- (5) BEAUCHAMP, C. E., AND LAZO, F. 1938 The composition of the alcoholic extract of cane leaves and its relationship with cane growth. *Proc. Ann. Conf. Assoc. Sugar Cane Technologists [Cuba]* 12: 1-14.
- (6) BEAUCHAMP, C. E. 1940 The mineral composition of the alcoholic extract of potato leaves and its relationship to crop yields. *Plant Physiol.* 15: 485-502.
- (7) BEAUCHAMP, C. E. 1942 Composition of alcoholic leaf extract and the entire leaf of Irish potatoes as indices of soil fertility. *Plant Physiol.* 17: 165-178.
- (8) BECKENBACH, J. R., WADLEIGH, C. H., AND SHIVE, J. W. 1936 Nutrition studies with corn. I. A statistical interpretation of the nutrient ion effect upon growth in artificial culture. *Soil Sci.* 41: 469-486.
- (9) BECKENBACH, J. R., ROBBINS, W. R., AND SHIVE, J. W. 1938 Nutrition studies with corn: II. A statistical interpretation of the relation between the ionic concentration of the culture solutions and the element content of the tissues. *Soil Sci.* 45: 403-426.
- (10) BROYER, T. C. 1939 Methods of tissue preparation for analysis in physiological studies with plants. *Bot. Rev.* 5: 531-545.
- (11) BRUNSTETTER, B. C., et al. 1939 A quantitative survey of eight mineral elements by a spectrographic method and of total nitrogen in young leaves of 25 varieties of American grapes. *Proc. Amer. Soc. Hort. Sci.* 37: 635-638.
- (12) BURKHART, L., AND PAGE, N. R. 1941 Mineral nutrient extraction and distribution in the peanut plant. *Jour. Amer. Soc. Agron.* 33: 743-755.
- (13) CAROLUS, R. L. 1927 The use of rapid chemical plant nutrient tests in fertilizer deficiency diagnosis and vegetable crop research. *Va. Truck Exp. Sta. Bul.* 98.
- (14) CHAPMAN, G. W. 1941 Leaf analysis and plant nutrition. *Soil Sci.* 52: 63-81.
- (15) CHAPMAN, H. D., AND BROWN, S. M. 1943 Potash in relation to citrus nutrition. *Soil Sci.* 55: 87-100.
- (16) CLEMENTS, H. F., MARTIN, J. P., AND MORIGUCHI, S. 1941 Composition of sugar cane plants grown in deficient nutrient solutions. *Hawaii. Planters' Rec.* 45: 227-239.
- (17) CLEMENTS, H. F., AND MORIGUCHI, S. 1942 Nitrogen and sugar cane. The nitrogen index and certain quantitative field aspects. *Hawaii. Planters' Rec.* 46: 163-190.

- (18) CLEMENTS, H. F., AND KUBOTA, T. 1943 The primary index, its meaning and application to crop management with special reference to sugar cane. *Hawaii. Planters' Rec.* 47: 257-298.
- (19) CULLINAN, F. P., AND WAUGH, J. G. 1939 Response of peach trees to potash under field conditions. *Proc. Amer. Soc. Hort. Sci.* 37: 87-94.
- (20) CULLINAN, F. P., AND RATJER, L. P. 1943 Nitrogen, phosphorus, and potassium interrelationships in young peach and apple trees. *Soil Sci.* 55: 49-60.
- (21) DROSDOFF, M. 1943 Fertilizing tung trees by leaf analysis. *Better Crops with Plant Food* 27 (4): 9-11.
- (22) DROSDOFF, M., AND PAINTER, J. F. 1942 A chlorosis and necrosis of tung leaves associated with low potassium content. *Proc. Amer. Soc. Hort. Sci.* 41: 45-51.
- (23) EMMERT, E. M. 1942 Plant tissue tests as a guide to fertilizer treatment of tomatoes. *Ky. Agr. Exp. Sta. Bul.* 430.
- (24) FUDGE, B. R. 1939 Relation of magnesium deficiency in grape fruit leaves to yield and chemical composition of fruit. *Fla. Agr. Exp. Sta. Tech. Bul.* 331.
- (25) GILBERT, B. E., AND HARDIN, L. J. 1927 The current mineral nutrient content of the plant solution as a possible means of chemical control of optimum fertilization. *Jour. Agr. Res.* 35: 185-192.
- (26) GOODHALL, D. W. 1943 Studies in the diagnosis of mineral deficiency: I. The distribution of certain cations in apple foliage in early autumn. *Jour. Pomol. and Hort. Sci.* 20: 137-143.
- (27) GREGORY, F. G. 1937 Mineral nutrition of plants. *Ann. Rev. Biochem.* 6: 557-578.
- (28) HALL, A. D. 1905 The analysis of the soil by means of the plant. *Jour. Agr. Sci.* 1: 65-88.
- (29) HARDY, F., MACDONALD, J. A., AND RODRIGUEZ, G. 1935 Leaf analysis as a means of diagnosing nutrient requirements of tropical orchard crops. *Jour. Agr. Sci.* 25: 610-627.
- (30) HESTER, J. B. 1941 Soil and plant tests as aids in soil fertility programs. *Com. Fert.* 63: 10-20.
- (31) HEINICKE, A. J., BOYNTON, D., AND REUTHER, W. 1939 Cork experimentally produced on Northern Spy apples. *Proc. Amer. Soc. Hort. Sci.* 37: 42-52.
- (32) HIBBARD, R. P. 1941 The detection, distribution, and mobility of certain elements in the tissues of plants growing under different conditions as determined by the spectrographic method. *Mich. Agr. Exp. Sta. Tech. Bul.* 176.
- (33) HOAGLAND, D. R., AND BROYER, T. E. 1936 General nature of the processes of salt accumulation by roots with description of experimental methods. *Plant Physiol.* 11: 471-507.
- (34) HOAGLAND, D. R., AND ARNON, D. I. 1941 Physiological aspects of availability of nutrients for plant growth. *Soil Sci.* 51: 431-444.
- (35) LAGATU, H., AND MAUME, L. 1927 Sur le contrôle chimique du mode d'alimentation de la vigne par les engrais. *Commun. Cong. Engrais Azotes de Synthèse à Montpellier.* (Juin) 1927. 1-15.
- (36) LAGATU, H., AND MAUME, L. 1930 Le diagnostic foliaire de la pomme de terre. *Ann. École Natl. Agr. Montpellier. Premier Mém.* 20: 219-281.
- (37) LAGATU, H., AND MAUME, L. 1932 Le diagnostic foliaire de la pomme de terre. *Ann. École Natl. Agr. Montpellier. Deuxième Mém.* 22: 50-126.
- (38) LAGATU, H., AND MAUME, L. 1938 La composition NPK des feuilles d'un rameau de vigne a-t-elle une relation avec celle du rameau est plus ou moins fructifère? *Compt. Rend. Acad. Sci. [Paris]* 207: 552-555.
- (39) LILLELAND, O., AND BROWN, J. G. 1938 The potassium nutrition of fruit trees: II. Leaf analysis. *Proc. Amer. Soc. Hort. Sci.* 36: 91-98.
- (40) LILLELAND, O., AND BROWN, J. G. 1939 The phosphate nutrition of fruit trees: II. Continued response to phosphate applied at the time of planting. *Proc. Amer. Soc. Hort. Sci.* 37: 53-57.

- (41) LILJELEND, O., AND BROWN, J. G. 1942 The phosphate nutrition of fruit trees: IV. The phosphate content of peach leaves from 130 orchards in California and some factors which may influence yield. *Proc. Amer. Soc. Hort. Sci.* 41: 1-10.
- (42) LINDNER, R. C., AND HARLEY, C. P. 1942 A rapid method for the determination of nitrogen in plant tissue. *Science* 96: 565-566.
- (43) LINDNER, R. C. 1944 Rapid methods for some of the more common inorganic constituents of plants. *Plant Physiol.* 19: 76-89.
- (44) LINDNER, R. C., AND HARLEY, C. P. 1944 Nutrient interrelations in lime induced chlorosis. *Plant Physiol.* 19: 404-434.
- (45) LOEWING, W. L. 1934 Physiological aspects of the effect of continuous aeration on plant growth. *Plant Physiol.* 9: 569-583.
- (46) LUNDEGÅRDH, H. 1938 The triple analysis method of testing soil fertility and probably crop reaction to fertilization. *Soil Sci.* 45: 147-54.
- (47) LUNDEGÅRDH, H. 1941 Die triple analyse. Theoretische und praktische Grundlagen einer pflanzenphysiologischen Method zur Bestimmung des Düngebedürfnisses des Ackerbodens. *Ann. Landw. Hochsch. Schwedens* 9: 127-221.
- (48) MACY, P. 1936 The quantitative mineral nutrient requirements of plants. *Plant Physiol.* 11: 749-764.
- (49) MAGOON, C. A., et al. 1938 A spectroscopic study of Concord and Ontario grape varieties. *Proc. Amer. Soc. Hort. Sci.* 36: 485-491.
- (50) MASON, T. G., AND PHYLIS, E. 1941 Studies on the partition of mineral elements in the cotton plant. II. Preliminary observations on potassium, calcium, and magnesium. *Mem. Cotton Res. Sta. Trinidad Ser. B* 14: 774-789.
- (51) MAUME, L., DULAC, C., AND BOUAT, A. 1934 Dosage rapide précis de N, P, K, Mg, Ca par semi-microanalyse. *Ann. École Natl. Agr. Montpellier.* 23: 5-43.
- (52) MITCHELL, H. L. 1935 A method for determining the nutrient needs of shade trees with special reference to phosphorus. *Black Rock Forest Papers* [Cornwall, N. Y.] 1: 1-3.
- (53) MITCHELL, H. L. 1936 Trends in the nitrogen, phosphorus, potassium, and calcium content of the leaves of some forest trees during the growing season. *Black Rock Forest Papers* [Cornwall, N. Y.] 1: 1-15.
- (54) NIGHTINGALE, G. T., AND SCHEERMLHORST, L. G. 1928 Nitrate assimilation by asparagus in the absence of light. *N. J. Agr. Exp. Sta. Bull.* 467.
- (55) NIGHTINGALE, G. T. 1942 Nitrate and carbohydrate reserves in relation to nitrogen nutrition of pineapple. *Bot. Gaz.* 103: 409-456.
- (56) NIGHTINGALE, G. T. 1943 Physiological-chemical functions of potassium in crop growth. *Soil Sci.* 55: 73-78.
- (57) PARKS, R. Z., et al. 1943 Quantitative chemical micro determination of twelve elements in plant tissue. *Indus. and Engin. Chem., Analyt. Ed.* 15: 527-533.
- (58) PETRIE, A. H. K. 1934 The drift of the content of potassium and calcium with age in plants. *Aust. Jour. Exp. Biol. and Med. Sci.* 12: 99-109.
- (59) PIPER, C. S. 1944 Analysis of Soils and Plants. Interscience Publishing Co., New York.
- (60) REUTHER, W., AND BOYNTON, D. 1939 Variations in the potassium content of the foliage from certain New York orchards. *Proc. Amer. Soc. Hort. Sci.* 37: 32-38.
- (61) RICHARDS, E. J. 1944 Mineral nutrition of plants. *Ann. Rev. Biochem.* 13: 611-630.
- (62) ROACH, W. A. 1939 Diagnosis of mineral deficiencies and excesses by systematic leaf injection and analysis. *Ann. Rept. East Mallory Res. Sta.* 1939: 51-58.
- (63) SCARSETH, G. D. 1943 Plant tissue testing in diagnosis of the nutritional status of growing plants. *Soil Sci.* 55: 113-120.
- (64) THOMAS, W. 1927 The seat of formation of amino acids in *Pyrus malus* L. *Science* 66: 115-116.
- (65) THOMAS, W. 1927 Nitrogenous metabolism of *Pyrus malus* L. *Plant Physiol.* 2: 109-137.

- (66) THOMAS, W. 1934 Misconceptions relative to the mineral composition of plants. *Science* 80: 587.
- (67) THOMAS, W. 1937 Foliar diagnosis: Principles and practice. *Plant Physiol.* 12: 571-600.
- (68) THOMAS, W. AND MACK, W. B. 1938 Foliar diagnosis in relation to the development and fertilizer treatment of the potato. *Jour. Agr. Res.* 57: 397-414.
- (69) THOMAS, W., AND MACK, W. B. 1940 Salient features of the method of foliar diagnosis. *Proc. Amer. Soc. Hort. Sci.* 37: 253-260.
- (70) THORNTON, J. F., CONNER, S. D., AND FRASER, R. R. 1939 The use of rapid chemical tests on soils and plants as aids in determining fertilizer requirements. *Purdue Agr. Exp. Sta. Cir.* 204 (Rev.).
- (71) TIEDJENS, V. A., AND BLAKE, M. A. 1932 Factors affecting the use of nitrate and ammonium nitrogen by apple trees. *N. J. Agr. Exp. Sta. Bul.* 547.
- (72) ULRICH, A. 1942 Potassium content of grape leaf petioles and blades contrasted with soil analysis as an indication of the potassium status of the plant. *Proc. Amer. Soc. Hort. Sci.* 41: 204-212.
- (73) ULRICH, A. 1943 Nitrate content of grape petioles as an indication of the nitrogen status of the plant. *Proc. Amer. Soc. Hort. Sci.* 41: 213-218.
- (74) ULRICH, A. 1943 Plant analysis as a diagnostic procedure. *Soil Sci.* 55: 101-112.
- (75) WALLACE, T., AND MANN, C. E. T. 1925 Investigations on chlorosis of fruit trees. 1. The composition of apple leaves in the case of lime-induced chlorosis. *Jour. Pomol. and Hort. Sci.* 5: 115-123.
- (76) WALLACE, T. 1928 The effects of manurial treatments on the chemical composition of gooseberry bushes: I. Effects on dry matter, ash, and ash constituents of leaves and stems of terminal shoots and of fruits and on total nitrogen of fruits. *Jour. Pomol. and Hort. Sci.* 7: 130-145.
- (77) WALLACE, T. 1928 The composition of leaves, bark, and wood of current season's shoots in cases of lime-induced chlorosis. *Jour. Pomol. and Hort. Sci.* 7: 172-183.
- (78) WALLACE, T. 1932 The nutrition of woody plants. *Forestry* 6: 1-26.
- (79) WALLACE, T. 1934 Some physiological disorders of fruit trees. *Ann. Appl. Biol.* 21: 322-333.
- (80) WALLACE, T. 1940 Chemical investigations relating to magnesium deficiency of fruit trees. *Jour. Pomol. and Hort. Sci.* 18: 145-160.
- (81) WANDER, I. W., AND GOURLEY, J. H. 1943 Effect of heavy mulch in an apple orchard upon several soil constituents and the mineral content of fruit and foliage. *Proc. Amer. Soc. Hort. Sci.* 42: 1-6.
- (82) WOLF, B. 1943 Rapid determination of soluble nutrients in soil and plant extracts. *Indus. and Engin. Chem. Analyt. Ed.* 15: 248-251.

THE pH OF SOIL SEPARATES

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The soil mass is composed of mineral particles varying from those of colloidal dimensions to those larger than gravel. Many of the physical and chemical properties of the soil vary with the physical and chemical properties of the soil separates, and on the whole their relative importance increases with decrease in particle size, reaching a maximum in the colloid fraction. In semiarid soils the minerals contributing to the alkaline reaction of the soil are limestone (caliche) and the group of minerals which manifest the property of base adsorption and exchange. All of these minerals exist in the soil as particles of varying dimensions. The contribution that these different sized particles make to the pII of the soil mass as a whole were studied, therefore, and the results are reported in this paper.

PREPARATION OF SEPARATES

For the preparation of the soil separates 500-gm. portions of 10 selected soils were worked, with 60 per cent methanol, in a mortar with a rubber pestle and washed, also with 60 per cent methanol, through a set of sieves of which the coarsest was 20 mesh (0.84 mm.) and the finest 100 mesh (0.149 mm.). The process of rubbing and washing was continued as long as any clay appeared in the washings. The soil passing through the 100-mesh sieve was further separated by sedimentation into clay (0.002 mm. and less), silt (0.002 to 0.02 mm.), and sand (0.02 to 0.149 mm.). Soils 1, 2, 3, 4, and 5 are alkaline-calcareous soils which contain no black alkali, 6 is a semiarid noncalcareous soil, 7 and K are black alkali soils, and R. I. and N. J. are acid soils.

pII OF SEPARATES

On all these separates, pII determinations were made, and the results are given in table 1. It is entirely possible that the base relations in the absorption complex were changed during the prolonged washing required for the particle separation, and this point should be recognized in interpreting the data. All salinity effects on pII are, of course, absent in these separates. The separates were stored for several months before the pII determinations were made. The data show that all the separates from the clay to those held by the 20-mesh sieve have pII values which are related more or less closely to the pH of the soil mass as a whole.

For the saline soils 1, 2, 3, 4, and 5, the pH values of the sand fractions are higher than those of the silt, and these, in turn, are higher than those of the clay for the determinations made both at a 1:10 soil:water ratio and at the moisture content represented by the moisture equivalent. The hydrolytic alkalinity in the silt and clay fractions, however, is greater than in the sand, as shown by

the greater difference between the pH at the moisture equivalent and at the 1:10 soil:water ratio. This is in harmony with data obtained in pH studies on soils naturally high in sand, silt, or clay particles.

For the noncalcareous soil, a semiarid mesa soil from which all the CaCO_3 has been leached into the lower soil horizons, a somewhat different condition exists. The pH values of the silt and clay fractions are higher than that of the sand at 1:10 soil:water ratio, but the pH value of the sand is highest at the moisture equivalent. The latter values therefore are in agreement with those for the calcareous soils. This indicates a difference in the hydrolytic pH of calcareous and noncalcareous soils. That is, for both the calcareous and the noncalcareous soils it is apparent that the finer soil particles possess the greater hydrolytic alkalinity. Though in this case it appears more evident in the non-

TABLE 1
pH values for soil particle separates at 1:10 soil: water ratio and soil paste or moisture equivalent

SIZE OF PARTICLE <i>mm</i>	PASTE		1:10		PASTE		1:10		PASTE		1:10		PASTE		1:10		PASTE		1:10	
	pH soil 1		pH soil 2		pH soil 3		pH soil 4		pH soil 5		pH soil 6		pH soil 7		pH soil K		pH soil R 1		pH soil N. J	
0.84	8.80	9.00	8.25	8.90	8.10	8.65	8.15	8.85			7.70	7.70	9.25	9.70	10.00	9.35	5.25	5.90	6.25	6.95
0.12 to 0.84	8.95	9.15	8.60	9.20	8.65	9.10	8.55	9.25	7.75	8.80	8.10	8.20	9.70	9.90	10.05	9.90	4.95	5.50	6.25	6.75
0.25 to 0.42	8.75	9.45	8.75	9.30	8.70	9.20	8.50	9.15			7.85	8.25	9.60	9.95	10.30	10.15	5.35	5.85	6.35	7.20
0.02 to 0.149	9.65	9.40	8.75	9.15	8.60	9.15	8.75	9.25	8.45	9.05	8.10	8.20	9.05	9.60	9.25	9.25	5.75	6.20	7.15	7.45
0.002 to 0.02	8.05	8.90	8.20	8.85	8.20	8.85	8.30	9.05	8.10	8.90	7.55	8.55	9.10	9.95	9.05	9.55	5.35	5.60	6.90	7.30
0.002	8.15	8.95	7.95	8.80	7.95	8.85	8.05	8.85	7.10	8.20	7.40	8.35	8.80	10.10	9.20	10.15	5.25	5.45	6.50	7.15

calcareous soil, this may not be true in all cases, for CaCO_3 has an appreciable hydrolytic alkalinity of itself.

The black alkali soils, 7 and K, exhibit particle-separate pH values different from those of both the calcareous and the noncalcareous soils in which black alkali is not present. Soil K, which is from the San Joaquin Valley in California, contains less CaCO_3 than the semiarid soils in Arizona. In fact, the coarse particles in this soil did not have any CaCO_3 present. The only fraction which effervesced with dilute HCl was the clay fraction. This probably explains the pH differences noted for the particles of sand and larger dimensions, namely, that the pH at the moisture equivalent is greater than the pH at 1:10 soil:water ratio. It is the only soil in the entire group that exhibits this property. It shows that the alkalinity of the coarse particles of soil K is so little that dilution to 1:10 reduced the OH-ion concentration to a point well below that at the

moisture equivalent. This is further indicated by the data given in table 2 showing the adsorption capacity of the soil separates and the effect of grinding. The black alkali soils differ from the types containing no black alkali in that the pH of the former at the 1:10 soil:water ratio increases from sand to silt, and from silt to clay. This is probably due to the greater amount of adsorbed sodium in these soil separates and to the presence of sodium carbonate. They also have a greater hydrolytic alkalinity, as shown by the difference between the pH of the soil paste and the pH at the 1:10 soil:water ratio in the clay fraction.

Soils N. J. and R. I., from New Jersey and Rhode Island respectively, were included in the group in order to provide a comparison with base-unsaturated

TABLE 2

pH of soil particle separates after saturation with Na, and adsorption capacity of separates

PARTICLE SIZE	mm	0.149- 0.84*	0.84	0.42- 0.84	0.25- 0.42	0.02- 0.149	0.002- 0.02	0.002
<i>Soil 6</i>								
At moisture equivalent	pH	9.00	8.90	8.60	9.20	9.65	8.90	8.30
At 1:10	pH	9.45	9.15	8.95	9.70	9.90	9.80	9.70
Adsorption capacity	m.e./100 gm.	4.0	0.3	0.8	1.9	1.9	13.9	27.9
<i>Soil 2</i>								
At moisture equivalent	pH	9.50	9.70			10.05	9.20	8.80
At 1:10	pH	10.35	10.25			10.20	10.25	10.10
Adsorption capacity	m.e./100 gm.	8.0	6.3			4.6	15.4	44.0
<i>Soil 3</i>								
At moisture equivalent	pH	9.60	9.10			9.90	9.20	8.75
At 1:10	pH	10.20	10.10			10.25	10.25	10.10
Adsorption capacity	m.e./100 gm.	3.2	2.2			3.4	7.50	45.00
<i>Soil 4</i>								
At moisture equivalent	pH	9.50	9.60			9.90	9.10	9.00
At 1:10	pH	10.20	10.15			10.10	10.10	10.10
Adsorption capacity	m.e./100 gm.	3.7	3.6			3.7	11.1	39.0
<i>Soil K</i>								
At moisture equivalent	pH	10.1	9.90			9.90	9.80	9.50
At 1:10	pH	10.1	9.90			10.30	10.30	10.40
Adsorption capacity	m.e./100 gm.	1.7	1.4			1.3	4.5	21.0

* Ground in ball mill to pass a 100-mesh sieve.

soils. It is interesting to note that the particle size-pH relationship is similar to that in the semiarid soils, namely, the pH is highest in the sand fraction and decreases toward the silt and clay fractions.

pH OF SODIUM-SATURATED SEPARATES

The soil separates from five of the soils were saturated with sodium, the cation which contributes most to the alkalinity of the adsorption complex in semiarid soils, and their pH values were determined. Sodium saturation was accomplished by leaching portions of the separates with normal NaCl solution in which the pH had been adjusted to 9.5 with NaOH and then washing with 60 per cent methanol until free from chloride. The pH values and the adsorp-

tion capacity for Na were determined. In order to have sufficient material for this, it was necessary to combine some of the coarse separates. The purpose in saturating these separates with a single base, preferably sodium, was to place them all on a comparable basis. The coarse soil separates, 0.149 to 0.84 mm., were also ground in a ball mill to pass a 100-mesh sieve, and pH and adsorption capacity were determined on these for comparison with the unground.

On grinding the coarse soil particles to less than 100-mesh, both the adsorption capacity and the pH were increased but not to the magnitude exhibited by the original soil fraction that passed the 100-mesh sieve. These data are given in table 2.

In a previous paper¹ it was shown that the pH of a sodium-saturated soil, at 1:10 soil:water ratio, is very nearly the same for all semiarid soils, regardless of the adsorption capacity in terms of milliequivalents per 100 gm. That is, a sandy soil with a low adsorption capacity has the same pH as a clay soil with a high adsorption capacity. The relation between the pH values and the adsorption capacities of the different soil separates, from 0.002 mm. to 0.84 mm., is in harmony with this relation noted in natural soils. For sodium-saturated soils at the moisture content represented by the moisture equivalent, it was found that the pH values are at a maximum in sandy soils and that the pH decreases with increase in percentage of clay (increase in adsorption capacity). The data given in table 2 are in harmony with this observation also. In every case, the pH of the sodium-saturated sand is higher than that of the sodium-saturated silt, which, in turn, is higher than that of the clay at the moisture equivalent.

SUMMARY AND CONCLUSIONS

The pH values obtained for the different soil separates at the moisture content represented by the moisture equivalent approximate, most closely those existing under field conditions. The data presented show that all soil separates exhibit pH values which closely approach the pH of the soil mass as a whole at this moisture content. Furthermore, the data show a close similarity between the pH values of soil separates from different soils, with slight variations from the average when black alkali is present or CaCO_3 is absent. The pH values at the moisture equivalent start low at 20 mesh, increase to a maximum for sand (0.02 to 0.149 mm.), and decrease again for the clay fraction. Hydrolytic alkalinity is greatest for the clay and least for the sand particles.

The data show that high pH values will be most easily produced in sandy soils under semiarid saline environment. Because of the low potential or hydrolytic alkalinity in such soils, their alkalinity should be least injurious to crops, and they should be most easily reclaimed. In silty or clay soils, the hydrolytic alkalinity being greater, the high pH should result in greater toxicity, partly because of this and partly because these soils are more strongly buffered by the greater colloid content. For the same reasons, these soils should be more difficult to reclaim.

¹ McGeorge, W. T. 1944 Base exchange-pH relationships in semiarid soils. *Soil Sci.* 59: 271.

THEORIES OF BASE-EXCHANGE EQUILIBRIUMS

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The concept of base-exchange equilibriums most generally accepted is clearly expressed thus by Magistad, Fireman, and Mabry (6). "It is believed that these reactions follow chemical laws and that definite equilibriums exist between the proportion of each cation on the exchange complex and the concentration of these cations in the soil solution." In particular, the authors assume that these reactions follow the law of mass action.

Theoretical and experimental studies of base-exchange equilibriums involving these concepts have been described by Gapon (2), Kerr (5), Magistad *et al.* (6), Marshall and Gupta (7), Vanselow (9), and others. Some workers, including Marshall and Gupta (7) and Jenny (3), have expressed doubt that base exchange can be described in terms of the law of mass action. Marshall and Gupta obtained data which did not agree with the mass-action concept when applied to any one of several mass-action equations proposed by various authors. Others have found that one or more of the equations which have been developed did not agree with their experimental results, particularly where ions of unequal charge were involved. On the other hand, Gapon, Kerr, Magistad *et al.*, Vanselow, and others have indicated satisfaction with the approximate degree of correspondence between one or the other equation and experimental results which they have obtained.

Several difficulties of a theoretical character are involved in the concept of base exchange as a chemical reaction which follows the law of mass action. Some of these difficulties have been noted by Marshall and Gupta (7). These authors have discussed Kerr's theory, which involves the coexistence of two types of clay at equilibrium, for example Na-clay and K-clay, when a suspension of one clay, *e.g.*, Na-clay, has been mixed with an electrolyte, *e.g.*, KCl. As these authors state, "The assumptions which must be made . . . are extremely numerous. In the thermodynamic sense the two clays are treated as though they exist independently in solution, behaving as weak electrolytes, while the concentrations of the cations are supposed to bear a constant relation to their thermodynamic activities." It may be remarked that these assumptions are probably formal; the clays are assumed to act *as though* they were independent entities, but it is not assumed that they *are* independent complexes.

Vanselow (9), Marshall and Gupta (7), and Magistad, Fireman, and Mabry (6) have recognized that a law of mass action can be strictly applied only to activities and not to concentrations of ions. It must be remarked that if an equation such as $\text{Na-clay} + \text{K}^+ \rightleftharpoons \text{K-clay} + \text{Na}^+$ could be considered as representing a chemical reaction, we should have to know the activities of each of the reactants to apply rigorously a law of mass action. The activities of K ions and Na ions in the filtrate can be calculated with certain assumptions, as Magistad

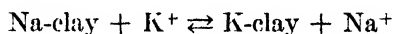
et al. did for NH_4 ions and Ca-clay, or measured directly as Marshall and Gupta did for H-clay and Tl ions. Marshall (8) recently introduced methods for measuring the activities of Na ions and K ions.

Vanselow did not attempt to measure the activities of the ions or the clays. However, he presented the hypothesis that the ratios of the activities of Na-clay and K-clay are proportional to the mole fractions of Na and K on the clay on the assumption that Na-, K-clay is a mixed crystal. He obtained data which apparently agreed with this hypothesis. Others have not been so successful in all cases.

On the other hand, Marshall and Gupta, accepting the concept that the clays are partly dissociated, have attempted to calculate the dissociation constants and the activities of the clays from measurements of the activities of ions both in the supernatant liquid and in the suspension residue. Davis (1) has shown that the interpretation of the concept of ionic activities is somewhat ambiguous and may be misleading. Marshall (8) has presented a good case for the value of measurements of ionic activities. Nevertheless, the utility of such measurements is limited. In particular the activity is not a measure of the true degree of dissociation, and only becomes approximately such a measure in the case of very weak electrolytes where the ionic concentration is extremely small. In the case of large multicharged particles, the activities of dissociated ions may be much more affected by the interaction (electrostatic and otherwise) between the dissociated ions and the charged particles than by the true degree of dissociation. If this is the case, the activities of the clays cannot be calculated from the measured activities of the dissociated ions. The results obtained by Marshall and Gupta are not in accord with the law of mass action, but, for the reasons just cited, it is not certain that they represent decisive arguments against the application of the mass-action concept.

Another assumption frequently made is that the hypothetical reactants, *e.g.*, Na-clay, dissociate to give a monobasic anion. Vanselow accepted this assumption and asserted that the data support the concept. In his theory, however, the anion is not a free ion but a crystal-lattice ion. This viewpoint is analogous to the concept postulated by Gapon (2) and Jenny (3) that exchange takes place at the single active spots, each with a single negative charge, on the clay particle.

More deep-seated objections to the concept of base exchange as a chemical reaction which follows the law of mass action should be considered. The experimental study of base exchange in a colloidal system involves the mixing of a colloidal electrolyte, for example, a suspension of Na-clay, with an ordinary electrolyte such as a solution of KCl, and a subsequent separation into a solution and a suspension residue by sedimentation or filtration. The results of the process may be expressed conveniently by the equation:



This equation is formally correct in the sense that it expresses the *fact* that Na ions are now found in a colloid-free solution, while some of the K ions remain in the residue, and that the exchange is stoichiometric. The equation may be *interpreted* to represent a definite chemical reaction which occurred upon mixing the

two ingredients. This interpretation is not necessarily valid unless we may assume that both K-clay and Na-clay are completely undissociated complexes. If both were completely dissociated, there would be no chemical reaction at all, just as the mixing of solutions of NaNO_3 and KCl does not lead to a chemical reaction. If either Na-clay or K-clay were partly dissociated, there would be a chemical reaction, but it would not be defined by analysis of the filtrate and the residue.

Very few, if any, colloidal materials which exhibit the property of base exchange are completely undissociated. Some may be completely dissociated. Others, particularly those which have replaceable cations inside the crystal lattice, as suggested by Marshall and Gupta, are partly dissociated.

A careful distinction must be made between (a) the dissociative equilibrium involving ions in the residue (or filtrate) and dissociated or undissociated clay; (b) the Donnan equilibrium, which involves the dissociated ions in the residue and filtrate; and (c) the base-exchange equilibrium. The last concept involves the relative numbers or activities of the ions (*e.g.*, K and Na) in the filtrate and the relative numbers or activities of *that fraction of the K and Na ions in the residue which are required to satisfy the charge on the colloidal complex*. Measurements of ionic activities in the suspension residue will not ordinarily yield these values. They are not related in any simple manner to the dissociative equilibrium, since they involve both dissociated and undissociated cations (if the latter are present).

The relative numbers of K and Na ions required to neutralize the charge in the colloidal complex cannot be measured in a suspension containing ordinary electrolytes. In fact any attempt to allocate Na and K ions to the colloid and to the ordinary anions must be fundamentally arbitrary. Jenny and Overstreet¹ have suggested, however, that this difficulty may be of minimum practical importance when the residue has been as completely freed as possible from the ordinary electrolytes by pressure filtration or centrifugal sedimentation.

Frequently the residue is washed with a nonhydrolyzing solvent and the relative amounts of Na and K in the electrolyte-free residue are determined. This material is not in thermodynamic contact with the original filtrate and is therefore not in equilibrium with it; therefore, a mass-action relation of a fundamental character cannot be expected for this case.

Under favorable conditions it is conceivable that the washed residue may be very approximately identical with the residue which might be left after removing as much free electrolyte as possible by pressure filtration. The base-exchange equilibrium may be considered provisionally as equivalent to a hypothetical model in which an electrolyte-free residue is in equilibrium with a filtrate.

The clay residue may be only partly dissociated, that is, some of the exchangeable ions of a given species may be dissociated and be present in the ion swarm, the liquid surrounding the particles, while some may be attached to the particle at any moment. Nevertheless, the escaping tendency of a given ionic species (consisting of both dissociated and undissociated ions) in the suspension residue will be equal to that for the same species in the filtrate. The escaping tendency

¹ Private communication.

will be a complex of contributing factors, which may be conveniently divided into three groups; (a) the tendency toward diffusion and dissociation as solely conditioned by ionic density in the diffuse double layer and on the particle, (b) the electrostatic potential in the double layer, and (c) a group of other factors due to hydration, wave mechanical forces, covalent bonds, etc.

The individual ionic activities, as ordinarily determined by electrometric measurements, eliminate the electrostatic potentials and are not identical with the escaping tendencies. Since the electrostatic potential is the same for all ions, however, the ratio of the ionic activities for two ions of the same charge are a measure of the relative escaping tendencies for the two ions. The ratio for the filtrate is, therefore, equal to that for the hypothetical residue. It follows that an expression having the form of a mass-action equation can be written for the ratios of the ionic activities and will be equivalent to the expression for the Donnan equilibrium in a system in which dissociation may be incomplete and in which the concentrations of mobile anions in the suspension residue are negligible. The constant in this equation will be unity. This case is not very interesting and, indeed, purely thermodynamic measurements are frequently more or less sterile.

An expression having the form of a mass-action equation can be written for the amounts (or concentrations) of ions in the residue and filtrate. The value of this expression will not necessarily be a constant when the relative concentrations are varied. If, however, under certain conditions, the third group of factors mentioned are approximately proportional, inversely, to the ionic densities, we might expect that the value for the mass-action expression would be approximately a constant.

Although there are no thermodynamic methods for considering this possibility, it seemed possible that a qualitative approach to the problem by the use of statistical mechanics might be of some help. The discussion that follows suggests the complexity of the state of affairs which probably exists in a colloidal suspension. It suggests further that no simple mass-action expression utilizing concentrations can be rigorously derived, but that by the use of certain assumptions, which are not purely formal or *ad hoc* but which may be considered as plausible, it can be shown that in certain cases the value of the mass-action expression may be expected to be approximately constant.

SIMPLE STATISTICS OF BASE-EXCHANGE EQUILIBRIUMS

The statistical method adopted is relatively simple and involves solely molar terms and ordinary coordinates. It is thus similar to the statistics utilized by Debye and Hückel in their theory of strong electrolytes. The method will first be applied to the equilibrium between a mixture of colloidal and ordinary electrolytes and a filtrate separated from the colloidal suspension. The thermodynamics of equilibria involved in Donnan systems containing a clay colloid and an electrolyte with a common cation has been discussed by Davis (1). The equilibria now under consideration involve a system of this type with two bases present. Later, the relationship between this type of equilibria and base-exchange equilibria will be considered.

In a system of this type, it should be necessary ideally for the external pressure to be different for the two phases. Since the osmotic pressure of colloids is very small, we may neglect this item. We may direct our attention to any two volume elements in the system, which are so small that the concentrations and potentials may be considered as uniform in the volume elements. Both of these volume elements may be in the same phase or one may be in each phase. Statistically, these two volume elements are in equilibrium. The escaping tendency of the ions must be the same for each volume element. The escaping tendency of ions may be expressed by the algebraic sum of two terms; (a) the diffusion energy of the ions as a function solely of their concentration, and (b) the potential energy of the ions in the potential fields present in the volume element.

Such equilibria may be characterized by the application of the familiar Boltzmann principle to the case of two spacially distinct volume elements, as may be done in the discussion of a gaseous atmosphere in a gravitational field, for example. Debye and Hückel utilized the Boltzmann principle in their theory of strong electrolytes, but the equilibrium was that between a somewhat hypothetical volume element close to any ion, as a central body, and an even more hypothetical volume element in which the ionic concentration was assumed to be equal to that of the system, taken as a whole.

Our attention may be confined now to the equilibrium between any volume element in the suspension phase and any volume element in the filtrate phase. The Boltzmann principle as it applies to each ionic species may then be expressed by the equation

$$n_i = n_i^0 e^{\frac{-e z_i (\psi - \psi^0) - (w_i - w_i^0)}{kT}} \quad (1)$$

where n_i and n_i^0 are the numbers of ions of the ionic species in question in the volume elements in the suspension and the filtrate, respectively; e is the base of natural logarithms; ϵ is the charge on a proton; z_i is the charge number (+ or -) of the ions in question; k is Boltzmann's constant, and T is the absolute temperature. The terms ψ and ψ^0 are the electrostatic potentials in the volume elements in the suspension and filtrate, respectively. We have also introduced terms, w_i and w_i^0 , representing the potential energy per ion which may be due to the concurrent effects of hydration, wave mechanical forces, mutual interaction between ions, ionic polarization, a van der Waals covolume factor, etc.

IONS OF EQUAL CHARGE

Donnan equilibria and ionic concentrations

Equation (1) represents a relation between ionic concentrations and potential energies in any single volume element in the residue and any single volume element in the filtrate. A similar relation can be derived for the two phases as a whole. The terms must first be redistributed to bring together concentrations and potential energies for each phase. A summation over the terms for the residue can then be taken while holding the terms for the filtrate constant. While this summation is held constant, a summation over the terms for the filtrate can then be taken.

After taking summations for both kinds of ions in the system and rearranging, we get an equation of the form

$$\frac{(\Sigma n_1)(\Sigma n_2^0)}{(\Sigma n_2)(\Sigma n_1^0)} = \frac{\Sigma e^{\frac{-(\epsilon z_1 \psi + w_1)}{kT}}}{\Sigma e^{\frac{-(\epsilon z_2 \psi + w_2)}{kT}}} \cdot \frac{\Sigma e^{\frac{-(\epsilon z_2 \psi^0 - w_2^0)}{kT}}}{\Sigma e^{\frac{-(\epsilon z_1 \psi^0 - w_1^0)}{kT}}} \quad (2)$$

Since the terms on the left of equation (2) are all in the first degree, the ratios of the summations are equivalent to ratios of concentrations in the two phases. Since $z_1 = z_2$, and ψ is the same for both ions, the electrical potential energy terms will be the same for both ions. If it were also true that $w_1 = w_2$ (and $w_1^0 = w_2^0$) in each volume element, the term on the right would be unity and equation (2) would represent the Donnan equilibrium for an ideal system.

Though we do not know explicitly very much about these other potential energy terms, we do know that ionic hydration energy, size of hydrated ions, polarization of ions, etc., are variable and, therefore, it is improbable that $w_1 = w_2$. If the ratios of the summations of the exponential terms for each ion in equation (2) were constant when the concentrations of electrolyte in the residue and filtrate are varied, we should have a mass-action equation for a Donnan equilibrium with a constant differing from unity. These ratios could only be constant, however, if w_1 and w_2 should differ by a constant. But since w_1 and w_2 differ from $z_1\psi$ and $z_2\psi$, in respect to the probability that the former will depend both upon properties of the ions which are different for the two ions and upon properties of the environment of the ions which vary with the environment, in general the two terms will not have a constant difference. Accordingly, we may expect the ratio on the right to vary with the number of ions present in the two phases. The mass-action equation for the Donnan equilibrium (where concentrations are involved) does not yield a constant.

Donnan equilibriums and ionic activities

Equation (1) may be rewritten in four different ways and summations may be taken as in the preceding paragraphs to yield expressions involving ratios equal to unity. One of these forms represents a thermodynamic concept in current usage and is derived from equation (1) when written in the form

$$(kT \ln n_i + w_i) + \epsilon z_i \psi = (kT \ln n_i^0 + w_i^0) + \epsilon z_i \psi^0 \quad (3)$$

We may subtract $kT \ln Nv$, where N is Avogadro's number and v is the volume element, from each side of (3) while multiplying all terms by N . One portion of each expression, e.g., $N(kT \ln n_i/Nv + w_i)$, represents the purely chemical potential energy of the ions per mole for each volume element. The ionic concentrations n_i/Nv are in moles per liter, if v is expressed in liters.

We may take the summation of the terms representing the suspension phase, keeping the terms representing the filtrate phase constant, but multiplying the latter by V/v where V is the volume of the suspension phase. After taking the summation over the filtrate phase, and rearranging, utilizing the multiplier

V^0/v where V^0 is the volume of the filtrate, we may take the difference between the two equations of this form for the two ionic species in the system. Since $z_1 = z_2$, the electrostatic potential energy terms are eliminated and the resulting expression becomes

$$\begin{aligned} \frac{Nv}{\bar{V}} \Sigma (kT \ln n_1/Nv + w_1) - \frac{Nv}{\bar{V}^0} \Sigma (kT \ln n_1^0/Nv + w_1^0) \\ - \frac{Nv}{\bar{V}} \Sigma (kT \ln n_2/Nv + w_2) + \frac{Nv}{\bar{V}^0} \Sigma (kT \ln n_2^0/Nv + w_2^0) = 0 \quad (4) \end{aligned}$$

An individual term, *e.g.*, $\frac{Nv}{\bar{V}} \Sigma (kT \ln n_1/Nv + w_1)$, represents the mean value of the ionic chemical potential energies per mole, or the value for the phase as a whole. The term is thus equal to the chemical potential of the ions, according to Gibbs, or to the chemical portion of the ionic partial molal free energy, F , of Lewis and Randall.

Since $F - F^0 = RT \ln a$, where F^0 is the partial molal free energy for the standard state, $R = Nk$ is the gas constant, and a is the activity, equation (4) may be transformed into the more easily recognized form

$$a_1 a_2^0 / a_2 a_1^0 = 1$$

The individual ionic activity coefficients, f_i , will be identified by the relations, $RT \ln f_i = \frac{Nv}{\bar{V}} w_i$, etc.

We have shown that the mass action law expression for Donnan equilibria may not provide a value K which is even approximately constant for ionic concentrations. On the other hand K is the constant unity for ionic activities. Our expectations are borne out by experimental evidence. In general it is well known, as shown by Davis (1), that the Donnan equilibrium equations can be applied only to ionic activities and not to concentrations.

Approximate character of base-exchange equations for ions of the same charge

Although mass-law equations for Donnan equilibria, involving concentrations of ions, do not yield constants, the results of any experiments described in the literature, particularly those dealing with ions of the same charge, have indicated fairly constant values of K for base-exchange equilibria. We shall see that some of the variables in the Donnan equilibria approach approximately constant values in base-exchange equilibria. It will also be seen quite clearly, however, that K is only approximately a constant.

We have suggested that the potential energy terms w_i depend upon certain properties of the ions and upon the environment. The environmental factor will be a function of the number and kinds of ions present in the volume element; in other words, it will depend upon the absolute number of both kinds of ions and also upon the relative numbers of each. When suspensions of an Na-clay, for example, are mixed with varying amounts of KCl, both the number of ions and

the relative amounts may vary greatly. We should expect w_i to have considerable variance in mixtures of this type before they are filtered and washed free of electrolyte.

On the other hand, in a washed residue, both the total number of ions and the number of charges will be unvariant when the ions are of equal charge, since these values depend solely upon the exchange capacity of the colloid and the amount of colloid present. The ratio of the numbers of each kind of ion may still be greatly variable, but we may reasonably expect that the environment will be determined by an additive effect of each kind of ion rather than by the ratio. The additive effect will be at a minimum in the washed residue where the variation of the number of each kind of ion is small.

We should expect these considerations to apply approximately to each volume element in the washed residue, although the total as well as the relative numbers of the ions in each volume element will probably vary with variation in the relative number of ions in the residue as a whole. (If K dominated in the residue, we should expect more ions near a particle surface than if Na dominated, for example.) Accordingly, w_1 and w_2 should be approximately constant.

If we may assume that the detached, washed residue may be represented by a hypothetical residue free from electrolyte but in equilibrium with the filtrate, the preceding considerations may be applied to the hypothetical system. In this case, since w_1 and w_2 are approximately constant, the ratio of the exponential terms for the residue in equation (2) will be approximately constant. The ratio of the exponential terms for the filtrate will not generally vary so much as those for an unwashed residue because the summation of the individual potential energy terms may be considered as very small. Since the discussion of the pure filtrate phase can be adequately covered by the method of Debye and Hückel, we need only remark that the preceding statement is equivalent to the assertion that the ratio of the activity coefficients of the two ions is more nearly a constant in the filtrate than in an unwashed residue. [We can, of course, eliminate the concentration and exponential terms for the filtrate and substitute the activities a_1^0 and a_2^0 on the left side of equation (2). But it should be remarked that if we applied this procedure also to the corresponding values for the hypothetical residue, the equilibrium constant would be unity, as we have seen.]

Since the right side of equation (2) when applied to our hypothetical system or to the relationship between the filtrate and the washed residue is approximately constant, we may, in a very loose sense, identify the equation with the usual equation found in the literature which has become known as Kerr's equation, for example

$$\frac{(\text{NaX})(\text{K})}{(\text{KX})(\text{Na})} = K \quad (5)$$

This equation is formally equivalent to the mass-law expression for equilibrium reactions between compounds of equal valence, *e.g.*, $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$. The hypothetical compounds NaX and KX apparently

behave like univalent compounds. Actually, it would seem that the resemblance is somewhat fortuitous. One need waste no concern over the fact that a particle with a multiple charge behaves like an ion with a single charge. In particular, the validity of the expression is not dependent upon the active charge spots being far enough apart to act as independent ions or upon whether there is a single dissociation constant.

IONS OF UNEQUAL CHARGE

Although most writers have developed equations identical with equation (5) for ions of equal charge, there is no general agreement in the case of ions of unequal charge. We can easily show that this situation is not surprising and that no single equation may be expected to fit all systems.

We shall discuss four conceivable equations of the mass-action law type. The first equation is identical with that for ions of equal charge, *i.e.*, it is equation (2). This equation has no proponents. The others may be identified, loosely speaking, with equations which have been proposed by Kerr, Gapon, and Vanselow, respectively.

In the case of ions of unequal charge, $z_1 \neq z_2$. The potential energy for an ion with charge number 2 is twice that for an ion with charge number 1. Accordingly, equation (2) cannot be expected to give a constant value. This difficulty could apparently be overcome by squaring the concentration and potential energy terms for the ions of charge number 1. A similar difficulty, however, will then be encountered with respect to the other potential energy terms w_1 and w_2 . Furthermore, the total number of ions present in the washed residue is no longer constant, because one ion with charge number 2 will replace two ions with charge number 1, and therefore the environment of the ions will vary with the relative numbers of the two kinds.

On the other hand, the variation in the number of ions on the clay after washing is only twofold between a pure Ca-clay and a pure Na-clay, for example. This is a much smaller variation than in the case of an unwashed suspension in which the total number of ions may vary between a few milliequivalents and several equivalents.

The summation over the suspension and filtrate for equation (1) would provide an equation of the same form as equation (1), *i.e.*, equation (2) where the summation for both ions is given. As we have seen, equation (2) is, loosely speaking, identical in significance with an equation like (5) representing the amounts or concentrations of ions. A summation of equation (1), after taking the square of all terms, will not provide an equation corresponding to measurable quantities, since $(\sum n_i)^2 > \sum (n_i)^2$; that is, the square of a sum of a series of numbers, is greater than the sum of the squares of the numbers. The term on the left represents the square of the number of ions of a given kind in the suspension residue, a measurable quantity; the term on the right cannot be determined. Instead of the inequality above, we may write the equation

$$(\sum n_i)^2 = \sum (n_i)^2 + p \quad (6)$$

where p is a quantity equal to twice the sum of a series of terms involving products of n_i for all pairs of volume elements in the suspension residue. A similar expansion will apply to the filtrate.

The relatively plausible assumptions which could be applied to the case of ions of equal charge cannot be so readily utilized for the case of ions of unequal charge. It seems probable that no simple equation for base-exchange equilibrium involving ions of unequal charge can rest very closely upon a sound theoretical basis. Furthermore, one may expect that no single equation will cover all cases or give values so nearly constant over a wide range of amounts of added electrolyte as for the case of ions of equal charge. It is not very surprising that different authors have set up widely different expressions, each of which represents a different theory of the mechanism of base exchange.

From the viewpoint presented in this paper, the approximate agreement between any one of these equations and the results of experiments is fortuitous in a more radical sense than for the case of ions of equal charge. Three types of equations may be analyzed in relation to this viewpoint. The conditions under which the equations may be expected to be most useful and the conditions under which they may be expected to fail will be discussed.

The equation developed by Kerr (5) is represented by the following expression:

$$\frac{(\text{NaX})(\text{Ca})}{(\text{CaX})(\text{Na})^2} = K \quad (7)$$

This equation is equivalent to

$$\frac{(\Sigma n_1)^2 (\Sigma n_2^0)}{(\Sigma n_2) (\Sigma n_2^0)^2} = \frac{[\Sigma (n_1)^2 + p] (\Sigma n_2^0)}{(\Sigma n_2) [\Sigma (n_1^0)^2 + p^0]} = K \quad (8)$$

We need not expand this equation in terms of the potential energy exponentials.

From the viewpoint of statistical mechanics, the fundamental equilibria are those represented by a pair of volume elements; for our purposes we are interested in the case of one volume element in the suspension residue and the other in the filtrate. It is probable that an expression involving simply the summation of the terms for the volume elements would yield a more nearly constant value than does equation (8). An equation of this type, of the general form of equation (8), is

$$\frac{\Sigma (n_1)^2 \cdot \Sigma n_2^0}{\Sigma n_2 \cdot \Sigma (n_1^0)^2} = K' \quad (9)$$

Equation (9) differs from equation (8) by inclusion in equation (8) of the terms p and p^0 , which will tend to make either the numerator or denominator increasingly larger than in equation (9) where either p or p^0 , is increased most rapidly. From equation (7), it will be seen that p will increase when NaX is increased, and p^0 will increase when Na in the filtrate is increased.

Equation (7) represents a base-exchange process in which varied amounts of a sodium salt are mixed with calcium clay. We should expect the smaller additions

of Na ions to be very greatly absorbed by the clay and p to increase, therefore, almost as rapidly as p^0 . On the other hand, when large amounts of Na ions are applied, p^0 will increase much more rapidly than p , and the denominator in (8) will increase rapidly. Thus for large additions of sodium salt, K , in equation (8), should decrease rapidly. Accordingly, we should expect that Kerr's equation will hold fairly well over a narrow range of small additions of sodium salt to a given amount of calcium clay, but that it may fail when large amounts are added.

Although we might expect that variations in the amount of clay would have small effects on the constancy of K' in equation (9), such variations will increase or decrease p (and p^0) as well as $\Sigma (n_1)^2$ and $\Sigma (n_1^0)^2$ and will thus tend to make K in equations (8) and (7) more variable. [This probability has been suggested by Vanselow (9) from an entirely different viewpoint.] If equal amounts of Na ions are added to increasing amounts of Ca-clay, p and therefore K should increase in value.

Kerr's equation was developed on theoretical grounds. Since it is approximately valid for a narrow range of varied concentrations of clay or added electrolyte, we may conceive that an identical equation could be derived empirically. We might then attempt to improve the equation (empirically) by the insertion of appropriate values. If we can find a term to insert in the denominator of equation (8) which will decrease as p^0 increases upon the addition of Na ions or which will increase as the amount of clay is increased while the amount of added Na is kept constant, the value of K will be maintained more nearly constant.

There are, no doubt, several possible means of improving equation (8) in this manner. We might insert the value (Σn_2) , equivalent to (CaX) . If we take the square root of all terms, we shall have an equation identical with that developed by Gapon (2) on theoretical grounds.

$$\frac{(\text{NaX})(\text{Ca})^{\frac{1}{2}}}{(\text{CaX})(\text{Na})} = K \quad (10)$$

We may expect Gapon's equation to be superior to Kerr's equation over a wide range of concentrations of Ca-clay or added Na ions.

A somewhat less drastic alteration of equation (8) could be effected by inserting a term $(\text{CaX} + \text{NaX})$, where CaX and NaX are expressed in millimols rather than in milliequivalents. The resulting equation will be identical in form with the equation developed by Vanselow (9) on a theoretical basis.

$$\frac{(\text{NaX})^2(\text{Ca})}{(\text{CaX})(\text{NaX} + \text{CaX})(\text{Na}^2)} = K \quad (11)$$

Where the amount of Na added to a given amount of Ca-clay is increased greatly, we may expect Gapon's equation to be more effective than Vanselow's equation, for the reason that when p^0 increases rapidly, upon increasing the added Na ions, NaX will increase also, and therefore the term $(\text{NaX} + \text{CaX})$ will not decrease but will in fact increase, since NaX will increase twice as fast as CaX decreases because two Na ions replace one calcium ion. On the other hand, when a given amount of Na is added to varied amounts of Ca-clay, Vanselow's

equation should be superior to Gapon's equation because the increase in p is more effectively counteracted.

In order to illustrate the principles discussed in the preceding paragraphs, equilibrium constant values have been calculated from data presented by Kerr (5), by Vanselow (9), and by Magistad, Fireman, and Mabry (6), comparing the expressions derived by Kerr, Vanselow, and Gapon (2). The results of these calculations are to be found in tables 1 to 7. Only the principal independent variables and the three constants are given. Gapon's equation has a purely arithme-

TABLE 1
Ca-NH₄ equilibria—quantity of soil constant
Data from Kerr (5), table 4, p. 396

EQUILIBRIUM, CONCENTRATION OF NH ₄ Cl	EQUILIBRIUM CONSTANTS		
	Kerr \sqrt{K}	Vanselow \sqrt{K}	Gapon K
<i>m.e./l.</i>			
2.40	0.276	0.118	0.100
3.80	0.278	0.118	0.104
5.27	0.283	0.117	0.109
6.83	0.274	0.113	0.109
8.33	0.274	0.110	0.112
9.93	0.278	0.110	0.117

TABLE 2
Ca-NH₄ equilibria—quantity of clay varied—NH₄ bentonite used
Data from Vanselow (9), table 8, page 106

INITIAL CONC. OF NH ₄	INITIAL CONC. OF Ca	INITIAL CONC OF NH ₄ Cl	KERR \sqrt{K}	VANSELOW \sqrt{K}	GAPON K
<i>m.e./l.</i>	<i>m.e./l.</i>	<i>m.e./l.</i>			
0.0	100.0	20.0	0.44	0.132	0.111
0.0	100.0	40.0	0.76	0.149	0.147
0.0	100.0	60.0	0.88	0.137	0.148
0.0	100.0	80.0	0.95	0.125	0.146
0.0	100.0	100.0	0.99	0.115	0.142
20.0	80.0	80.0	0.91	0.116	0.147
40.0	60.0	60.0	0.82	0.117	0.178
60.0	40.0	40.0	0.69	0.120	0.212
80.0	20.0	20.0	0.46	0.107	0.259

tic advantage, since the squares of a series of values diverge more rapidly than the values themselves. In order to make the variation of the constants more comparable, the square roots of the constants according to Kerr and Vanselow are presented. Also for convenience in comparison, in all cases the base-exchange reaction is taken to be written in the direction $n \text{ NH}_4^+ + \text{Ca}_m \text{ X} \rightleftharpoons \text{NH}_4_n \text{ X} + m \text{ Ca}^{++}$ so that the quantities on the right always appear in the numerator. The values given in the tables may thus be reciprocals of those presented by the authors in some cases.

TABLE 3
Ca-NH₄ equilibria—quantity of clay varied—Ca-bentonite used
 Data from Vanselow (9), table 9, page 107

INITIAL CONC. OF NH ₄	INITIAL CONC. OF Ca	INITIAL CONC. OF CaZ ₂	KERR \sqrt{K}	VANSELOW \sqrt{K}	GAPON K
<i>m.e./l.</i>	<i>m.e./l.</i>	<i>m.e./l.</i>			
20.0	80.0	20	0.294	0.088	0.070
40.0	60.0	40	0.377	0.077	0.067
60.0	40.0	60	0.482	0.078	0.074
80.0	20.0	80	0.550	0.075	0.078
100.0	0.0	100	0.645	0.077	0.086
100.0	0.0	80	0.578	0.076	0.090
100.0	0.0	60	0.526	0.078	0.101
100.0	0.0	40	0.456	0.080	0.120
100.0	0.0	20	0.323	0.078	0.152

TABLE 4
Ca-NH₄ equilibria quantity of clay constant—mixed Ca and NH₄ clays used
 Data from Vanselow (9), table 10, page 109

INITIAL CONCENTRATIONS				EQUILIBRIUM CONSTANTS		
NH ₄ Z	CaZ ₂	NH ₄	Ca	Kerr \sqrt{K}	Vanselow \sqrt{K}	Gapon K
<i>m.e./l.</i>	<i>m.e./l.</i>	<i>m.e./l.</i>	<i>m.e./l.</i>			
0.0	100.0	69.8	30.1	0.697	0.087	0.084
0.0	100.0	99.8	0.0	0.662	0.079	0.087
30.0	70.0	99.8	0.0	0.671	0.076	0.104
60.0	40.0	99.8	0.0	0.675	0.074	0.130

TABLE 5
Na-Ca equilibrium—amount of soil constant—Ca-Fallbrook sandy loam used—solutions contained Ca + Na = 10 m.e./l.

Data from Magistad, *et al.* (6), table 1, page 375

Na IN ORIGINAL SOLUTION	EQUILIBRIUM CONSTANTS		
	Kerr \sqrt{K}	Vanselow \sqrt{K}	Gapon K
<i>per cent</i>			
50	0.0510	0.0195	0.0099
80	0.0466	0.0179	0.0095
90	0.0465	0.0179	0.0095
95	0.0456	0.0176	0.0094
98	0.0431	0.0166	0.0090
100	0.0426	0.0167	0.0090

It is clear that none of the three equations is superior to the others in all cases. The inadequacy of Kerr's equation in the case where the amount of colloid is

varied appears evident from tables 2, 3, and 6B. The results in table 7, where the range of variation of Σn_1^0 (NH_4 ion in the filtrate) is very great, show the effect of the increase in the value of this term in all cases. This effect, as we have an-

TABLE 6

Na-Ca equilibrium—Fallbrook sandy loam used—solutions contained 27 m.e./l. of NaCl and 3 m.e./l. CaCl_2

Data from Magistad, *et al.* (6), table 2, page 376

VOLUME OR WEIGHT	EQUILIBRIUM CONSTANTS		
	Kerr \sqrt{K}	Vanselow \sqrt{K}	Gapon K
A—Volume varied, 25 gm. soil			
<i>ml.</i>			
25	0.0217	0.0152	0.0079
50	0.0212	0.0148	0.0079
125	0.0197	0.0148	0.0077
500	0.0220	0.0158	0.0089
1000	0.0207	0.0145	0.0084
2500	0.0212	0.0145	0.0085
B—Amount of soil varied, volume 500 ml.			
<i>gm.</i>			
5	0.0086	0.0141	0.0080
15	0.0152	0.0138	0.0078
50	0.0276	0.0134	0.0076
100	0.0367	0.0130	0.0071

TABLE 7

Equilibrium data originally from Gedroiz, reported by Gapon (2) and recalculated by Magistad, et al.—Tula chernozum used—amount of soil and volume of solution constant— NH_4Cl concentration of solution varied

Data reported by Magistad, *et al.* (6), table 3, page 377

CONCENTRATION OF NH_4Cl	EQUILIBRIUM CONSTANTS		
	Kerr \sqrt{K}	Vanselow \sqrt{K}	Gapon K
<i>equiv./l.</i>			
0.01	0.121	0.086	0.0148
0.05	0.124	0.082	0.0165
0.10	0.118	0.063	0.0171
0.50	0.087	0.049	0.0179
1.00	0.066	0.034	0.0163
2.00	0.041	0.022	0.0112
4.00	0.030	0.017	0.0102

ticipated, is modified most greatly by Gapon's equation, less by Vanselow's, and least by Kerr's.

The data supplied by Vanselow are very important. Besides illustrating the

significance of studying variation of K with amounts of soil, Vanselow has also shown the effect of hysteresis. The value of K appears to be larger whenever the ion originally on the clay appears in the numerator. Vanselow has shown that this cannot be due to insufficient time to reach equilibrium.

CONCLUSIONS

Base-exchange equilibria, as ordinarily defined, are not identical with Donnan equilibria. When a system containing colloidal clay, two cationic species, and one or more anionic species is filtered, the filtrate may be a phase in Donnan equilibrium with the suspension residue phase. The two phases constitute an intact thermodynamic system. We may say, in a rigorously thermodynamic sense, that each of the ionic species in the filtrate phase is in equilibrium with those in the suspension residue phase.

If the suspension residue phase is washed to remove all excess electrolyte, the remaining ions may be said to be on the colloid. But the washed material is a separate system from the original filtrate. The two systems are not phases of an intact thermodynamic system and cannot be said to be in equilibrium. The relationship between the ions left on the colloid after washing and those left in the original filtrate is frequently called a base-exchange equilibrium. It seems clear that it is not a true equilibrium, however.

On the other hand, the number of cations of each species left in the suspension residue before it is washed may be arbitrarily divided into those which are said to be on the colloid and those which are not. The relationship between those which are said to be on the colloid and those in the filtrate (or between those said to be on the colloid and those in suspension phase which are not considered on the colloid) is also usually considered as a base-exchange equilibrium. Inasmuch as no completely defined reaction has actually occurred and many of the ions cannot be described as either on the clay or not on the clay but are simply in the continuous ion swarms surrounding the particles, the meaning of the concept of base-exchange equilibrium is not entirely clear.

When a solution of NaCl is mixed with a suspension of K-clay, for example, no well-defined reaction occurs and it is meaningless to say that base-exchange has taken place with regard to the fraction of the ions which are dissociated. There will, of course, be a redistribution of the K-ion concentration as a function of distance from the particles. If the suspension is filtered, no chemical reaction will occur during this process. We can now say, however, that base exchange has taken place and that the two phases are in equilibrium. Also, the ions are in equilibrium. We may properly say that we have equilibrium in a two-phase system which has been prepared by a process involving base exchange. The equations of the mass-action law type which have been derived by several workers for the relation between the ions on the colloid and those not on the colloid are arbitrary expressions and not expressions of definite chemical laws. They may, however, have an approximate validity in favorable cases. They may be considered either as approximately derived from more general expressions or perhaps even as primarily empirical equations.

In addition to the theoretical importance of studies of base-exchange equilibria, the agricultural importance should be again emphasized as it has been by many authors. The application of the principles involved should be carefully considered, however. When K and Ca are added to a soil in the form of fertilizers or soil amendments, they tend to replace preferentially Na and Mg and also to replace H more readily than do Na or Mg. The availability of these ions is probably not greatly affected, particularly in view of the concept of contact exchange feeding of plants as developed by Jenny and Overstreet (4). On the other hand, these effects become very important when moderate leaching by rain or careful irrigation removes the excess electrolyte without markedly affecting the exchange complex, as may be the case in the moderately arid regions of the Southwest. Again, in more humid regions or where excessive irrigation with fresh mountain water and good drainage are factors, so that the equilibria are progressively shifted, the marked tendency of H-ion to replace bases may become the factor of predominating interest.

SUMMARY

The significance of the concept of base-exchange equilibria is critically analyzed. The relation between the ions assumed to be on the colloid and those not on the colloid (in the soil solution or in a filtrate) is usually supposed to involve a chemical equilibrium which can be expressed by an equation of the mass-action law type.

It is shown that these ideas are incompletely defined and that the entire concept of base-exchange equilibrium as a true thermodynamic equilibrium is not entirely valid.

Equilibria between colloidal suspensions containing salts of two cations and filtrates obtained from such suspensions are discussed theoretically. The equilibria are Donnan equilibria. The treatment is based upon the application of Boltzmann's principle to equilibria between very small volume elements in the suspension and in the filtrate. The equilibrium relations between the two complete phases are then derived. On theoretical grounds, mass-action law equations for the Donnan equilibria should not yield equilibrium values that are constant, when the variables are concentrations, but solely when the variables are activities.

These Donnan systems involve true equilibria between two phases, the preparation of which has involved a base exchange. However, these equilibria are not identical with the usual concept of base-exchange equilibria.

Reasons are given why "equilibrium constants," with *approximately* constant values, may be expected, theoretically, for equations which are formally of the mass-action law type and which express the base-exchange relation between ionic concentrations for ions of the same charge.

Four base-exchange equations for the case of ions of unequal charge are discussed. The validity of each equation, as judged by the constancy of the "equilibrium constant," varies with concentration of electrolyte and colloid in the suspension. A theoretical explanation of these facts is developed. The sig-

nificance of this explanation is indicated by calculations based on data presented in the literature by various authors.

REFERENCES

- (1) DAVIS, L. E. 1942 Significance of Donnan equilibria for soil colloidal systems. *Soil Sci.* 54: 199-219.
- (2) GAPON, E. N. 1933 On the theory of exchange adsorption in soils. *Jour. Gen. Chem.* [U. S. S. R.] 3: 141-163.
- (3) JENNY, H. 1936 Simple kinetic theory of ionic exchange. I. Ions of equal valency. *Jour. Phys. Chem.* 40: 501-517.
- (4) JENNY, H., AND OVERSTREET, R. 1939 Surface migration of ions and contact exchange. *Jour. Phys. Chem.* 43: 1185-1196.
- (5) KERR, H. W. 1928 The identification and composition of the soil aluminosilicate active in base exchange and soil acidity. *Soil Sci.* 26: 384-398.
- (6) MAGISTAD, O. C., FIREMAN, M., AND MABRY, B.: 1944 Comparison of base-exchange equations founded on the law of mass action. *Soil Sci.* 57: 371-379.
- (7) MARSHALL, C. E., AND GUPTA, R. S. 1933 Base-exchange equilibria in clays. *Jour. Soc. Chem. Indus* 52: 433-443.
- (8) MARSHALL, C. E. 1944 The uses and limitations of membrane electrodes. *Jour. Phys. Chem.* 48: 67-75.
- (9) VANSELOW, A. P. 1932 Equilibria of the base-exchange reactions of bentonites, permutites, soil colloids, and zeolites. *Soil Sci.* 33: 95-113.

CUP CONDUCTANCE, FIELD AND LABORATORY CALIBRATION OF TENSIOMETERS EMPLOYING INEXPENSIVE POROUS CUPS

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In the fall of 1941 a research program that required the use of some means of checking on the utilization of soil moisture by apple trees was designed. Tensiometers or soil moisture meters were deemed the most desirable instrument for this purpose. The design of tensiometers published by Richards, Russell, and Neal (2) was considered too costly. Stoeckeler and Aamodt (5) used a design that was rather inexpensive and a porous cup which was made of "flower pot clay" and cost only a fraction of the price charged for more expensive clay cups or filters. This cup, however, was not of the proper size for insertion in the soil by means of the sampling tube best adapted to this study.

The cups used in this study were obtained² at a catalogue price of 16 cents each. They were 25 mm. in diameter and 76 mm. in height and had a variable wall thickness. The total cost of constructing the tensiometers, not including the mercury, was approximately 50 to 75 cents. The purpose of this paper is to present data demonstrating the possibility of using this inexpensive cup on a tensiometer and to illustrate the influence of soil capillary saturation point upon the characteristics of the calibration curve.

CUP CONDUCTANCE

The rate of flow of water through the porous cup determines the speed of reaction of the tensiometer to fluctuations in soil moisture. Since this is a very important feature of the porous cup, the conductance was determined on several of the inexpensive cups selected.

Figure 1 illustrates the arrangement of the equipment used to determine cup conductance. The presence of air in the system was found not only to cause considerable fluctuation in the values obtained but also to give exceedingly high values. When a very small quantity of air was present anywhere in the system, the readings obtained were much higher than those obtained with an air-free system. The pump used to decrease pressure in the system was capable of pulling 68 cm. of mercury. The water used had a maximum instant tension of 66 cm. Boiled distilled water was used in all cases.

The cups were soaked in water at room temperature at least overnight, then boiled in distilled water to remove all air. After the cups had been cooled in distilled water of the same temperature as that used in the system, they were inserted in the beaker of water shown in figure 1. The connection to the suction

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pump was removed, and by means of a hand pump the water in the suction flask was forced out through the mercury well. Connection was made with the suction pump and a tension of 66 cm. was drawn on the system until the water column above the cup had broken. The tension was released and the system checked for the presence of air. The water above the mercury in the mercury well was pipetted off. The screw clamp was closed and suction applied to the suction flask. The screw clamp was released until a tension of over 50 cm. (55–60 cm.) was shown in the mercury column. By means of a stop watch the time required for the mercury to fall from 50 cm. to 10 cm. was recorded. The tension was applied three times to every cup, and an average of the three readings was used in the calculation of cup conductance K_{20} .

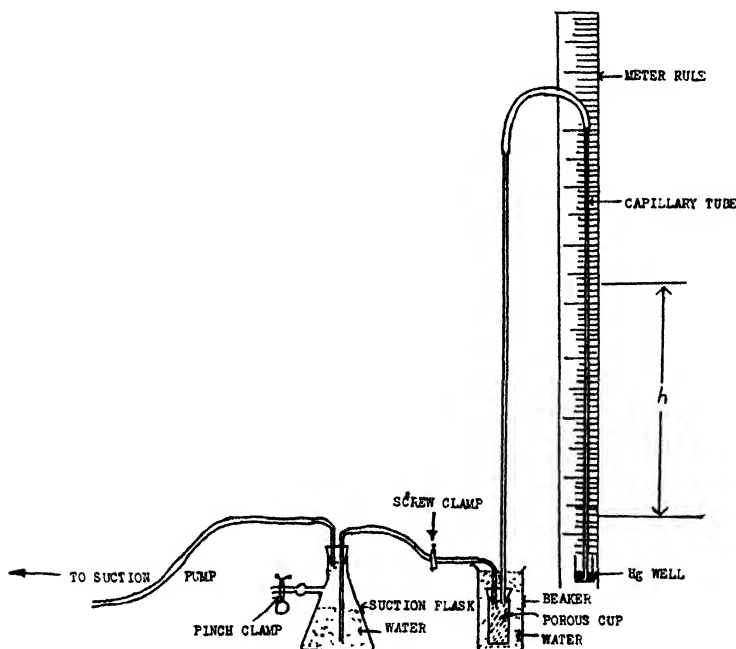


FIG. 1. APPARATUS FOR DETERMINING CUP CONDUCTANCE

Cup conductance was calculated by the method of Richards, Russell, and Neal (2). The conductance values presented in table 1 were obtained on 50 cups.

The average value of K_{20} for these 50 unselected cups was found to be 0.024 with a range of 0.012 to 0.035. These values of conductance are lower than the values (av. 0.053) reported by Richards, Russell, and Neal (2) but essentially the same as the average value for the cups described by Richards (3).

Richards (3) reported that the air entry value for porous cups has a reciprocal relation to the conductance values and, further, the air entry value should be over 2 atmospheres. On the basis of the conductance and air entry values presented by him, it appears safe to conclude that the air entry values for the cups used in the foregoing conductance test would be adequately high.

FIELD CALIBRATION

On August 25, 1941, 60 tensiometers using the cups described were installed in the irrigation orchard at the Irrigation Branch Experiment Station (Prosser, Washington). The orchard was planted in Sagemoor fine sandy loam. The plots employed were irrigated with applications of 3, 5, 6, and 10 acre-inches per acre. Tensiometers were installed at 1-, 2-, and 3-foot depths midway between the irrigation furrows, which were 24 inches apart.

TABLE 1
*Conductance of porous cups**

CUP NUMBER	<i>l</i>	<i>K</i> ₃₀	CUP NUMBER	<i>l</i>	<i>K</i> ₃₀
	<i>seconds</i>	<i>cc. atmo. -1 sec. -1</i>		<i>seconds</i>	<i>cc. atmo. -1 sec. -1</i>
1	76.0	0.012	26	33.5	0.027
2	59.0	0.016	27	29.0	0.032
3	29.5	0.031	28	51.0	0.018
4	53.5	0.017	29	33.5	0.027
5	54.0	0.017	30	42.0	0.022
6	49.0	0.019	31	38.0	0.024
7	56.0	0.016	32	32.0	0.029
8	56.0	0.016	33	34.0	0.029
9	58.0	0.016	34	31.5	0.029
10	53.5	0.017	35	29.0	0.032
11	58.0	0.016	36	42.0	0.022
12	37.5	0.025	37	26.5	0.035
13	48.0	0.019	38	32.5	0.028
14	54.0	0.017	39	33.0	0.028
15	52.0	0.018	40	32.0	0.028
16	41.5	0.022	41	30.0	0.031
17	56.0	0.016	42	32.0	0.029
18	67.0	0.014	43	27.0	0.034
19	38.0	0.024	44	34.5	0.027
20	49.5	0.019	45	50.5	0.018
21	27.5	0.033	46	28.0	0.033
22	31.0	0.030	47	27.0	0.034
23	28.5	0.032	48	40.0	0.023
24	31.5	0.029	49	36.5	0.025
25	36.5	0.025	50	42.5	0.022

* $n = 0.0101$; $h = 40$ cm.; $A = 0.0069$ sq. cm.

On September 2, 4, 6, 8, 11, 13, 14, and 17 the soil in the immediate vicinity of these tensiometers was sampled for moisture determinations. Sampling was done just before and 24 hours after irrigation of a plot. The sample used for soil moisture determinations was taken with a soil tube, and the soil from 6 inches above to 6 inches below the level of the center of the cup was used for the moisture determination. Duplicate samples were taken for each tensiometer. The pre-irrigation samples were taken 6 inches from the tensiometer; and the postirrigation samples, 12 inches from the tensiometer. At the time of sampling, a reading was made on the tensiometer and the cup tension was calculated. The data ob-

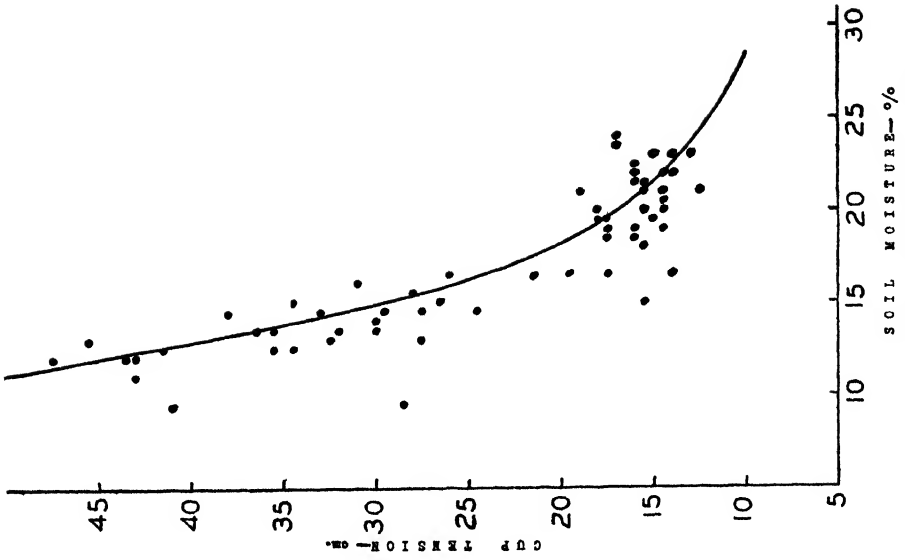


FIG. 2. FIELD CALIBRATION OF TENSIO METER AT THE 1-FOOT DEPTH

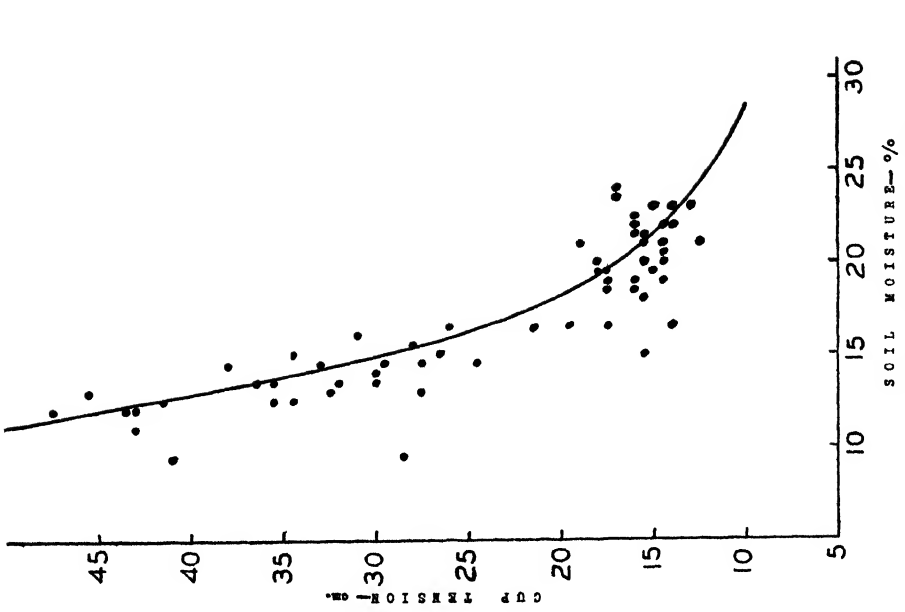


FIG. 3. FIELD CALIBRATION OF TENSIO METER AT THE 2-FOOT DEPTH

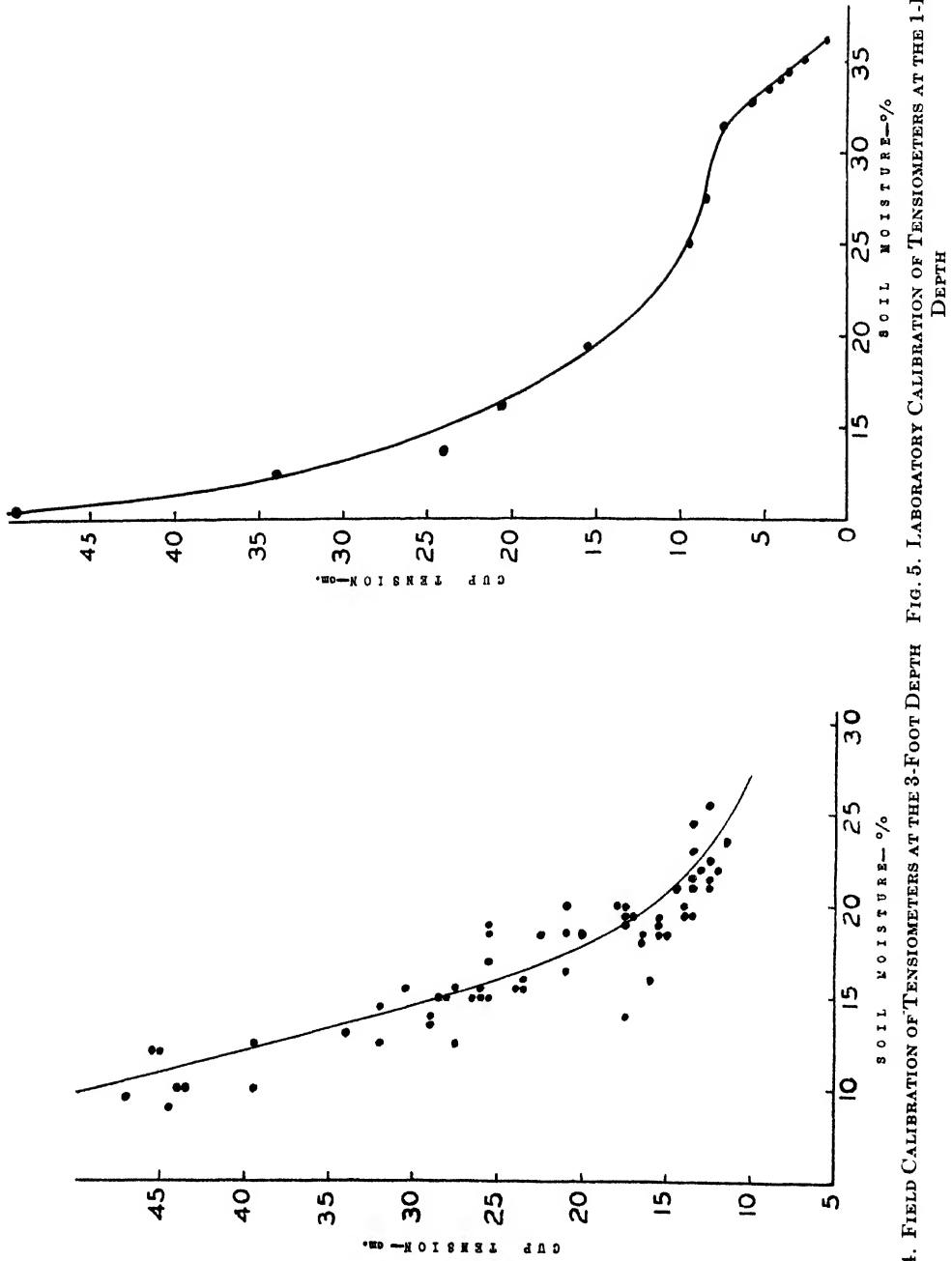


FIG. 4. FIELD CALIBRATION OF TENSIO-METERS AT THE 3-FOOT DEPTH FIG. 5. LABORATORY CALIBRATION OF TENSIO-METERS AT THE 1-FOOT DEPTH

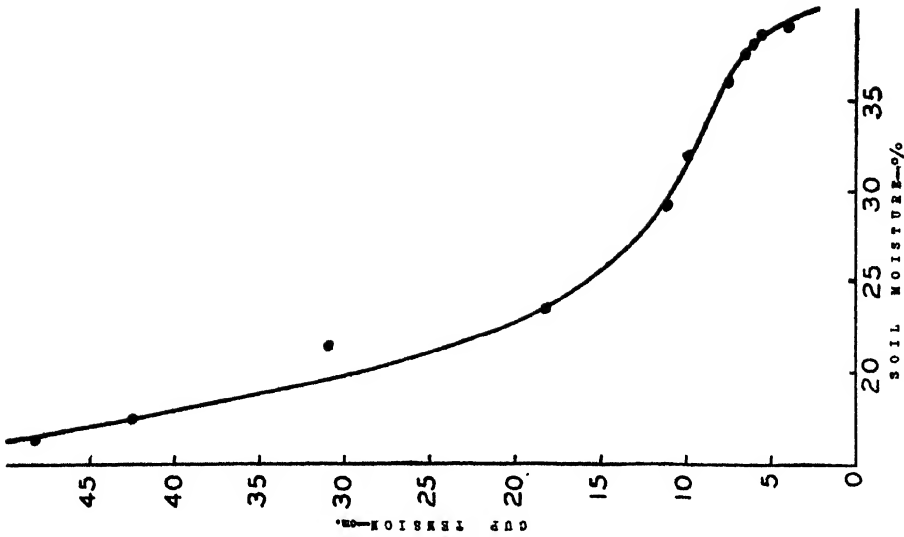


FIG. 7. LABORATORY CALIBRATION OF TENSIO-METERS AT THE 3-FOOT DEPTH

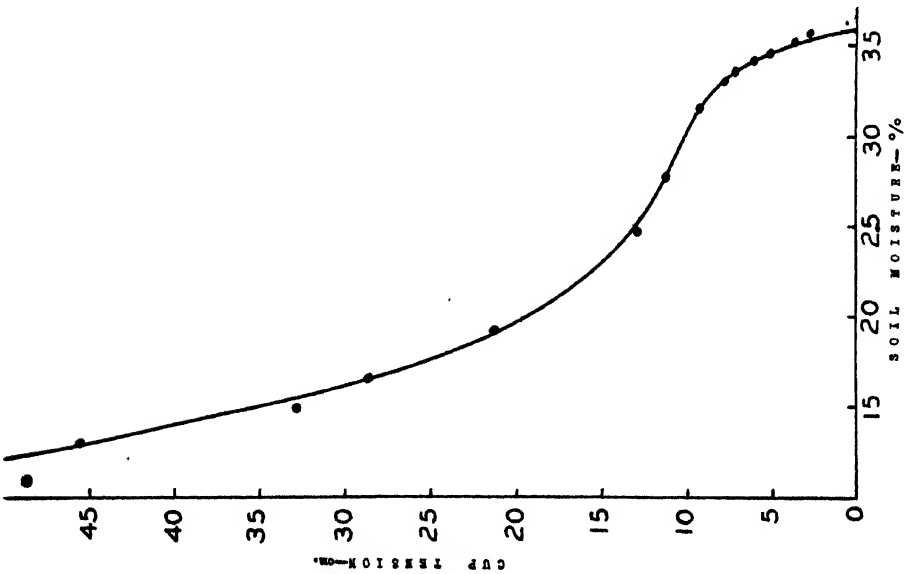


FIG. 6. LABORATORY CALIBRATION OF TENSIO-METERS AT THE 2-FOOT DEPTH

tained in this manner are presented in figures 2, 3, and 4, showing the relationship between cup tension and soil moisture at the three depths.

LABORATORY CALIBRATION

When the tensiometers were installed in the orchard, the volume of soil replaced by the cup was saved and a composite sample from the 60 installations was used for laboratory calibration purposes. Laboratory calibration was conducted by filling a no. 3 tin can (drainage provided) with the soil and embedding a porous cup therein. The porous cup was then connected with a mercury manometer having a mm. tube. The soil was then wetted from the surface and the soil allowed to dry at room temperature. Frequent readings were made on the height of the mercury column, and the entire system was weighed at the same time. When the limit of mercury tension was reached the percentage of moisture in the soil was determined. From these readings and determinations, cup tension and percentage of moisture in the soil were determined. In figures 5, 6, and 7 are presented the curves resulting from the data obtained in this manner.

DISCUSSION

The close similarity between the curves resulting from the calibration for the three depths is very striking. The soil in which the tensiometers were installed carried considerable organic matter in the first foot of soil, and the third foot commonly contained a thin hardpan. The soil at all depths had a low clay content. As may be noted, the curve for the second-foot depth (figs. 3, 6) shows a higher percentage moisture at a given cup tension than does the curve for the first-foot depth (figs. 2, 5). This is not in agreement with the findings of Stoeckeler and Aamodt (5) that, with increased organic matter, a curve resulted that showed a higher percentage of soil moisture for a given tension. In the field calibrations the curve for the third-foot depth (fig. 4) falls between those of the first- and second-foot depths (figs. 2, 3). This was not the case with the laboratory calibrations. The laboratory calibrations show that the third-foot depth had a higher percentage of moisture at a given tension than did the second-foot depth, which shows a similar relationship to the first-foot depth.

The discrepancy between the laboratory-calibration curve and the field-calibration curve for the second and third foot of soil may be due to the removal of large gravel-like particles and hard impervious calcareous sections of the soil prior to laboratory calibration.

The sharp bend in the curves for laboratory calibration as the capillary saturation point is reached is of interest. The moisture equivalent of these soils as determined by the suction method (1) was approximately 30 per cent. The calibration curves break and show decline sharply just after this percentage of moisture is reached. This sharp decline in the curve is apparently the result of free water in the soil mass. This characteristic is not shown by Stoeckeler and Aamodt (5) or by Rogers (4) for soils containing considerable clay and loam, and is not present in a curve obtained by the author on another study conducted on composted soil containing loam and peat. Rogers (4), however, presents a curve

for sand that shows the same sharp decline in tension as those presented in figures 5, 6, and 7. This curve shows this sharp decline occurring in sand when the tension was approximately 2.5 cm. and the soil moisture was 18 per cent. This characteristic of a calibration curve will probably not result from soils containing more clay and silt.

The tensiometers used in this study would reestablish equilibrium within 6 hours after refilling with water at a tension of 45 cm., and continuous daily readings have been obtained from them for over a period of 3 months.

SUMMARY

The inexpensive porous cups used in this study appear to be satisfactory for use on tensiometers. A close similarity exists between the field and laboratory calibration curves obtained by use of the cups. A sharp decline in the tension appears to result when free water occurs in Sagemoor fine sandy loam.

REFERENCES

- (1) BOUYOUCOUS, G. J. 1935 A comparison between the suction method and the centrifuge method for determining the moisture equivalent of soils. *Soil Sci.* 40: 165-171.
- (2) RICHARDS, L. A., RUSSELL, M. B., AND NEAL, Q. R. 1937 Further developments on apparatus for field moisture studies. *Soil Sci. Soc. Amer. Proc.* 42: 55-66.
- (3) RICHARDS, L. A. 1941 Soil moisture tensiometer materials and construction. U. S. Regional Salinity Laboratory, B.P.I., Riverside, Calif., Memo. Rept., June 26.
- (4) ROGERS, W. S. 1935 A soil moisture meter depending on the capillary pull of the soil. *Jour. Agr. Sci.* 25: 326-343.
- (5) STOECKELER, J. H., AND AAMODT, E. 1940 Use of tensiometers in regulating water in forest nurseries. *Plant Physiol.* 15: 589-607.

THE WATER TABLE, EQUIPOTENTIALS, AND STREAMLINES IN DRAINED LAND: III

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In arriving at the results presented in parts I and II of this series (2, 3) the assumption was made, following precedent and buttressed with general arguments, that uniformly distributed rainfall arrives at the boundary of the capillary fringe (or at the water table if the fringe is ignored) having maintained uniformity of distribution, so that the rate at which water flows across any element of the fringe boundary is proportional to the area of the projection of that element on a horizontal plane. The purpose of this paper is to discuss how far this assumption is justified and to investigate the magnitude of the error introduced in the stream picture when the assumption is invalid. To avoid repetition of cumbersome phraseology, in what follows the above type of flow distribution at the capillary fringe boundary will be referred to as "uniform distribution," although that description should really be reserved for circumstances in which the rate of flow across any element of the boundary is proportional to the area of the element itself, and not to its projection.

The subject may be introduced most simply by considering a vertical soil column of uniform physical constitution and cross section, with its lower end at a depth d below a plane water surface. We may plot the potential ϕ against the height h to give a diagram such as figure 1, ϕ being defined as hitherto, namely,

$$\phi = p + g\rho h \quad (1)$$

h being measured from the level of the plane water surface, atmospheric pressure being the hydrostatic pressure datum, and g and ρ having their usual meanings. For static equilibrium ϕ is everywhere zero and the potential distribution is therefore represented by the h axis, DWS in figure 1, where W is the origin. Let WB be the straight line

$$\phi = g\rho h \quad (2)$$

and let FC be the straight line

$$\phi = p_c + g\rho h \quad (3)$$

where p_c is the pressure defining the upper boundary of the capillary fringe (3). Since p_c is negative, FC is parallel to WB and a vertical distance $|p_c|$ below it. Corresponding to any point on the diagram, the pressure is given by the vertical distance above the line WB ; for all points above the line FC the pressure is greater than p_c and the soil is sensibly saturated, whereas for all points below FC the pressure is less than p_c and the soil is unsaturated. For static equilibrium

column is unsaturated. The potential distribution curve cannot proceed beyond F' with concave curvature to the h axis (*i.e.*, with negative $d^2\phi/dh^2$), for this would imply an increase of permeability with a decrease of pressure and, by inference, of moisture content, which is inconsistent with the known behavior of porous media. It is even unlikely that the curve should proceed in the same straight line beyond F' , since, of the dozen soils so far examined and reported upon, only one, described as Greenville loam (8), exhibits the inexplicable characteristic of almost constant permeability over a considerable range of moisture content. We may accept the principle, therefore, that for any ordinary soil the curve at F' must be convex to the h axis. For the same reason it must continue to be convex until the slope becomes equal to that of WB , which occurs at H , say. Beyond H the curve can continue only as a straight line parallel to WB , since the previous argument rules out concavity to the h axis, and convexity implies a decrease of permeability with increase of pressure, which again is inconsistent with the known facts. Hence above H the potential gradient is uniform at its maximum value, independent of both the nature of the soil and the rate of flow, and is given by the equation

$$d\phi/d = g\rho \quad (5)$$

It follows that in this zone the pressure, moisture content, and permeability are also uniform, but at minimum values as compared with any other part of the column for the same flow rate. For a given effective velocity u we may calculate the permeability, k_{\min} , above H by combining equations (4) and (5), whence

$$k_{\min} = -u/(g\rho) \quad (6)$$

Let p_{\min} be the hydrostatic pressure at which the soil permeability assumes the value k_{\min} ; then HS' is a part of a straight line parallel to WB and a vertical distance $|p_{\min}|$ below it. The extent of the convex portion, *i.e.*, the location of H , remains to be discussed.

The pore-size distribution in the soil determines to a high degree the shape of the soil moisture characteristic (1) and therefore the relationship between pressure and permeability. If the pores are virtually uniform in size, the moisture content, and the permeability with it, will fall from the maximum value at pressure p_e to very low values at pressures but little less than p_e . For all rates of flow accommodated by values of k_{\min} within the range covered without appreciable fall of pressure below p_e , the line HS' can never fall far below FC . We must therefore have some such potential distribution as is represented by the curve $DW''F''S''$, which may reasonably be described as two straight lines intersecting at F'' . The location of the water table is represented by W'' and that of the capillary fringe boundary by F'' . If the rate of flow is increased, the curve changes to $DW'''F'''S'''$, the potential gradient increasing in the saturated region, as it must do, the permeability being constant at k_{\max} , and the water table and capillary fringe rising to new heights W''' and F''' , while the potential gradient in the unsaturated region remains unaltered at $g\rho$, the increased flow rate being accommodated by an increase of moisture content giving a new,

higher value of k_{\min} with but an imperceptible pressure change. For a soil with a greater range of pore sizes, the permeability may not be reduced to k_{\min} without an appreciable reduction of pressure below p_c . The convex part of the potential distribution curve, therefore, may be extensive, indicating the presence of a zone of appreciable thickness in which there is a gradation of permeability between the two limits k_{\max} and k_{\min} . The change of permeability seems generally to be most sudden for pressures in the neighborhood of p_c (4, 8, 9), as is to be expected, since the largest pores, which are emptied with the least reduction of pressure, are those which contribute preponderantly to k_{\max} . The most abrupt change of permeability must therefore usually occur at the upper boundary of the capillary fringe. We may note in passing that k_{\max} is a soil constant and is independent of rate of flow, whereas k_{\min} depends only on the rate of flow, as shown by equation (6), and is the same for all soils in similar circumstances.

Let us now apply these conclusions to our drainage problem. We may at first imagine the flow between the soil surface and the capillary fringe boundary to be constrained artificially into vertical paths by the division of the unsaturated zone into a large number of vertical tubes of flow separated by impermeable walls, the tubes being of small and uniform cross section. Uniform distribution of rainfall at the surface is, of course, a general assumption in all these problems, so that u is the same for all the tubes. Let h be measured as usual from the level of free water in the drain, at which p is zero. Consider first the case of soil with very nearly uniform pore sizes. The potential gradient above the capillary fringe, *i.e.*, throughout each isolated tube, is given by equation (5), whereas the potential at the base of any given tube, *i.e.*, at the capillary fringe boundary upon which that tube abuts, at height h' , say, is given by (3) with h' substituted for h . Hence at height h in any tube the potential is given by

$$\begin{aligned}\phi &= p_c + g\rho h' + \int_{h'}^h g\rho \, dh \\ &= p_c + g\rho h\end{aligned}\tag{7}$$

Hence the equipotentials throughout the unsaturated zone are horizontal planes continuous through the impermeable tube walls; these walls may therefore be removed without disturbing the stream picture. Thus we have proved that in the unsaturated zone of such soil the equipotentials are horizontal planes and the streamlines are truly vertical, as has hitherto been assumed.

Uniformity of pore sizes is the exception in agricultural land. For soils of more usual type, with a zone of gradation of permeability, we may write for the potential gradient up any particular isolated tube

$$d\phi/dh = g\rho - f(h)\tag{8}$$

where $f(h)$ is a positive function which decreases as height increases, and becomes zero at and above a height λ above the capillary fringe boundary upon which the tube abuts. The potential at height h in any tube then becomes

$$\begin{aligned}
 \phi &= p_c + g\rho h' + \int_{h'}^h \{g\rho - f(h)\} dh \\
 &= p_c + g\rho h - \int_{h'}^h f(h) dh
 \end{aligned}
 \tag{9}$$

If the range of integration exceeds λ , (9) becomes

$$\begin{aligned}
 \phi &= p_c + g\rho h - \int_{h'}^{h'+\lambda} f(h) dh - \int_{h'+\lambda}^h f(h) dh \\
 &= p_c + g\rho h - K
 \end{aligned}
 \tag{10}$$

where K , the integral over the range λ , is the same for every tube; the integral over any range beyond λ is zero, since the integrand is zero. Equation (10) shows that the equipotentials are horizontal planes, continuous through the tube walls, in that part of the unsaturated zone which lies at a greater distance than λ above the capillary fringe and where the potential gradient is $g\rho$ and the permeability therefore k_{min} . In this region the walls may be removed without disturbing the stream picture. For points less than λ above the capillary fringe, the integral on the right hand side of equation (9) differs for different tubes at the same height h , hence the equipotentials are not continuous through the tube walls, in the absence of which we may not assume the streamlines to be vertical. We must use the method of electric analogues to see what shape the streamlines really have. But first we may point out that, given two stream pictures which are similar as regards the configuration of boundaries, water table, and saturated zone equipotentials, but which differ in flux density because of different soil permeabilities, the value of the ratio k_{max}/k_{min} is the same for both, since both, in common with all soils, have the same equipotential configuration also in the region of k_{min} . We have shown that the streamlines are truly vertical in that part of the unsaturated region where the permeability, k , is equal to k_{min} ; hence, for a stream picture of given configuration the departure of k_{max}/k in any region from the value k_{max}/k_{min} is an indication of the deviation of the streamlines from the vertical.

EXPERIMENTAL METHOD

For simplicity we shall confine ourselves, as usual, to the case of equidistant parallel drain lines of infinite length and uniform depth, the drains being just filled with water in order to ensure that the drain perimeter shall be an equipotential (see parts I and II). The electric analogue showing the stream picture for a cross section perpendicular to the drain lines is a sheet conductor with boundaries representing, to scale, the impermeable floor, the soil surface, a vertical plane through one drain line, and another plane parallel to this last and at a distance d from it, where the drain separation is $2d$. Current is fed in at the surface (not at the capillary fringe or the water table, as hitherto) with uniform distribution to represent uniformly distributed rainfall, and is led out at an electrode representing the drain. The conditions to be satisfied, by trial and

error, may best be explained by supposing the analogue to have been successfully constructed.

Corresponding to the water-table profile, which satisfies equation (2), there will be a locus of points satisfying the equation

$$V = Ah \quad (11)$$

where V is the electric potential and A is a constant which expresses the scale according to which V represents ϕ . If the linear scale of the analogue is $I:N$, then a point on the water table analogue at height h and potential V represents a point on the water table at height Nh and potential ϕ given by

$$\phi = g\rho Nh \quad (12)$$

Hence from (11) and (12) we have

$$\phi/V = g\rho N/A \quad (13)$$

Corresponding to the profile of the capillary fringe boundary, satisfying (3), there will be a locus of points satisfying

$$V = Ah - C \quad (14)$$

where C is a positive constant related to p_c as follows. Corresponding to a point at height h on the analogue of the capillary fringe boundary, at which the potential V is given by (14), there is a point at height Nh on the fringe boundary in the soil, at which the potential ϕ , as given by (3), is

$$\phi = g\rho Nh + p_c \quad (15)$$

But, combining (13) and (14), we have

$$\begin{aligned} \phi &= (Ah - C)(g\rho N/A) \\ &= g\rho Nh - g\rho NC/A \end{aligned} \quad (16)$$

Hence, comparing (15) with (16), we have the required relation

$$p_c/C = -g\rho N/A \quad (17)$$

In a similar manner we can show that the pressure p at any point in the soil is related to the potential V at the corresponding point in the analogue by the equation

$$p = g\rho N\{(V/A) - h\} \quad (18)$$

At any point below the capillary fringe boundary the permeability is constant at the saturation value, k_{\max} ; hence the electrical conductivity in the corresponding region of the analogue must be uniform, say μ_{\max} ; the actual value may be chosen freely, since the scale by which current density in the analogue represents water-flux density in the soil is not preassigned. At any point above the capillary fringe, the conductivity μ of the analogue must be connected with the permeability k at the corresponding point in the soil by the relation

$$\mu/\mu_{\max} = k/k_{\max} \quad (19)$$

where k must also conform to the requirement that it be the permeability appropriate to the pressure p as calculated from (18).

In the work described here, variations of conductivity were obtained by preparing a sheet of nominally uniform conductivity in the usual way and painting different parts of it appropriately with diluted "Aquadag" colloidal graphite. It will easily be realized that the production of a reasonably true analogue of a given soil would be laborious and is not necessary for the study of principles. It is easier to be satisfied with an analogue which is consistent in itself and to let the physical characteristics of the corresponding soil emerge with the solution.

EXPERIMENTAL RESULTS

The first set of experiments was designed to show the deviation from the vertical of the streamlines in the unsaturated zone for different values of k_{\max}/k . Figure 2 depicts the case in which the potential gradient changes abruptly to the value $g\rho$ in the upper zone, *i.e.*, the case of a soil with uniform pore sizes. The equipotentials are sensibly horizontal and the streamlines vertical above the capillary fringe, except for some distortion in the upper right hand corner of the diagram, distortion which is clearly due to locally excessive conductivity of the analogue. The capillary fringe boundary separates two zones of sensibly uniform permeability, and this stream picture serves to determine the ratio k_{\max}/k_{\min} for this particular configuration of boundaries, water table, and capillary fringe; the value of this ratio is 5.0. In the production of this and the following analogues, the height of the fringe boundary at the midpoint was arbitrarily chosen and the remainder of the boundary was adjusted to satisfy equation (14), with both parameters A and C available for free choice to ensure the best possible fit. Both A and C being thus determined, the water table was automatically located. Earlier procedure was to fix A and C separately, the former by arbitrarily fixing one point on the water table and the latter by selecting a point on the fringe boundary, in those cases where the fringe was not ignored. The change of procedure was adopted because of the difficulty of correcting errors in the analogue in the present work, since local "touching up" by painting with graphite can rarely be carried out well enough to ensure continuity with the already painted area. Correction of error usually involved making a fresh start, and the additional freedom afforded by the admissibility of choosing two parameters was invaluable, although of course the resulting stream picture was less firmly under control than hitherto.

Figure 3 depicts a case in which k_{\max}/k is only 3.0, the capillary fringe boundary again separating regions of different uniform permeabilities. The capillary fringe boundary is much the same as in figure 2, but because of the lower degree of control described above, the fringe thickness is somewhat different, as also is the value of p_0 . This hardly matters, since the two pictures obviously refer to two different soils in any case, and we are seeking no comparison other than that between the shape of the streamlines above the saturated zone for two different values of k_{\max}/k .

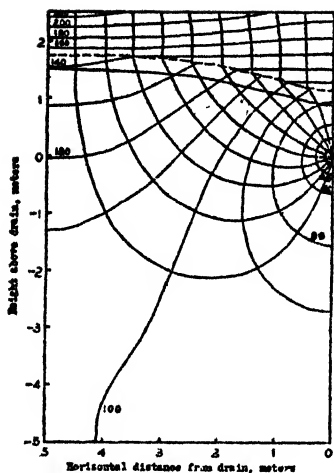


FIG. 2

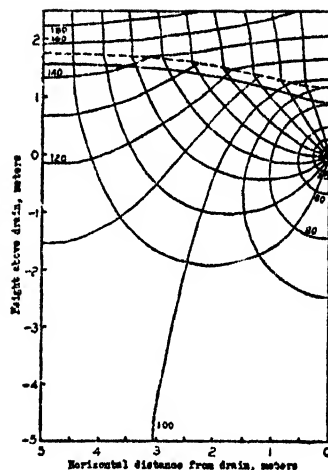


FIG. 3

FIG. 2. STREAM PICTURE FOR A PARTICULAR CASE OF DRAINED LAND, WITH PERMEABILITY BELOW THE CAPILLARY FRINGE FIVE TIMES THAT ABOVE

Unit of potential, 1000 ergs per cubic centimeter

FIG. 3. SIMILAR TO FIGURE 2, BUT PERMEABILITY BELOW THE CAPILLARY FRINGE ONLY THIRCE THAT ABOVE

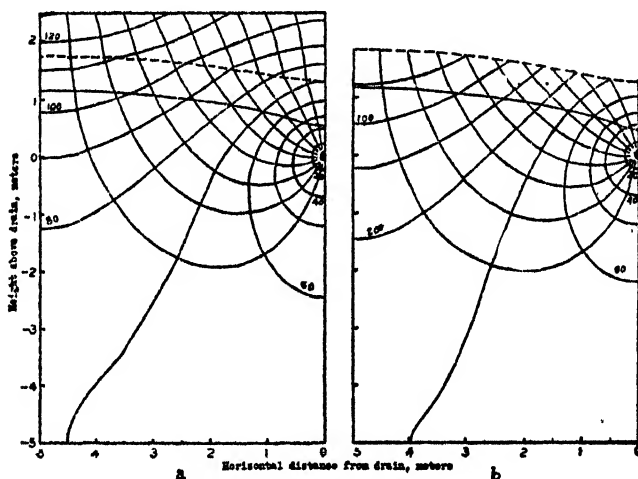


FIG. 4. COMPARISON BETWEEN THE WATER TABLE AND CAPILLARY FRINGE

a. When the permeability below the capillary fringe boundary is only slightly greater than that above.

b. For similar circumstances except that the streamlines above the capillary fringe are assumed to be vertical.

Unit of potential, 1000 ergs per cubic centimeter.

A third picture was obtained with k_{\max}/k equal to 7.3 for the sake of continuity of the series. It is not reproduced, since it involves a potential gradient in the unsaturated zone greater than $g\rho$, which cannot occur. The streamlines differed

as little from those of figure 2 as do those of figure 3, but naturally in the opposite sense.

In figure 4a, which refers to a second experiment, and which differs somewhat from the foregoing as regards the water-table configuration, the permeabilities in the two zones differ by no more than is required to define a boundary (k_{\max}/k equals 1.23), and in this case only do the streamlines in the unsaturated zone depart appreciably from vertical straight lines.

It is so much simpler to assume the flux distribution at the fringe boundary to be uniform and to proceed by the technique of part I that it becomes important to know what magnitude of error is involved in so doing. Figure 4 presents a comparison between (a) a stream picture obtained by the method described in the present paper, with permeability variations as described briefly above, and with streamlines above the ground water which deviate from the vertical by amounts that can hardly be much exceeded in any circumstances, and (b) the stream picture for the saturated zone alone, assuming uniform flux distribution at the boundary of the capillary fringe, all other conditions remaining unchanged.

DISCUSSION

Little need be said about figure 2. Since it shows approximately uniform potential gradient of $g\rho$ in the unsaturated zone, it provides us with the value of k_{\max}/k_{\min} for this particular configuration of boundaries and water table; the value of this ratio is 5.0. This configuration is sufficiently similar to that of figure 3 to warrant the assumption that the same value of k_{\max}/k_{\min} is appropriate for the two figures. The actual value of k_{\max}/k for figure 3 is only 3.0, *i.e.*, the arithmetic mean of the limiting values 1.0 and 5.0. Since the permeability above the capillary fringe is uniform at a value greater than k_{\min} , a word of justification is required, since such a soil would have the unusual property of constant permeability, intermediate between k_{\max} and k_{\min} , for a wide range of pressures less than p_c . Not even the anomalous Greenville loam previously mentioned has this characteristic. Now, examination of figure 3 shows that nowhere at the surface is the pressure greater than about -40 cm. of water, and an examination of published information (4, 8, 9) shows that this pressure is generally sufficient to reduce the permeability to one fifth of k_{\max} , *i.e.*, to the lower limiting value for our particular configuration. Moreover, since for most soils the permeability decreases most abruptly within a few centimeters of the capillary fringe boundary, so that the lower values of k have greater weight than the higher values in determining the average permeability over the unsaturated zone, it is likely that the arithmetic mean of the limits of k_{\max}/k is an underestimate of that average. Hence our value of k_{\max}/k in figure 3, regarded as an average over the unsaturated zone, is more likely than not to be an underestimate of that occurring in any given soil for this particular configuration of boundaries and water table, and the deviation of the upper streamlines from the vertical, slight as it is, is quite likely to be more than in any practical case, insofar as one may permit such generalizations on the basis of rather few soils

examined. Since k_{\max}/k cannot in any circumstances be less than 1.0, figure 4a shows the extreme of deviation from the vertical possible for the configuration.

From the point of view of practical drainage we are primarily concerned with the effect of divergence or convergence of the upper streamlines on the shape of the capillary fringe boundary. The concentration or dispersal of flux at this boundary depends on the lengths of the tubes of flow as well as upon their angles of convergence or divergence; great length of path, however, clearly does not lead to proportionately great departure from uniformity of distribution at the fringe boundary, since the streamlines have been shown to become vertical above a certain height, at which the potential gradient becomes $g\rho$. Figure 4a shows as extreme a case of nonuniformity of flux distribution at the capillary fringe as can be imagined. The low value of k_{\max}/k results in great deviation of the upper streamlines from the vertical, though the depth of drains is as great as would ever be likely to occur in practice, giving a depth of unsaturated soil which provides such scope for the dispersal or concentration of flux as cannot often be exceeded in the field. Regarding figure 4a as the true stream picture, we see that the simpler procedure of parts I and II, resulting in figure 4b, leads to an overestimation of the height of the water table and capillary fringe midway between neighboring drains, and a compensating underestimation immediately over the drainlines. This is to be expected, since the artificial constraint of the upper streamlines into vertical paths increases the flux density at the capillary fringe between the drains and reduces it over the drains. Both errors are, however, so slight that they may reasonably be regarded as unimportant for practical purposes. Moreover, the agriculturally important factor is the highest point of the saturated zone, namely, midway between the drains, and figure 4 shows that the simplified procedure overestimates this; such error as there may be is therefore on the safe side.

SUMMARY

It is shown that the streamlines above the capillary fringe in soil with sensibly uniform pore sizes are truly vertical, justifying assumptions made in preceding work. Stream pictures obtained by the method of electric analogues show that, in more usual soil types, the streamlines above the capillary fringe do not depart very much from the vertical, and even where the departure is the maximum which can commonly occur in practice, the error introduced into drainage calculations by assuming them to be vertical is not serious, and is in any case on the safe side.

REFERENCES

- (1) CHILDS, E. C. 1940 The use of soil moisture characteristics in soil studies. *Soil Sci.* 50: 239-252.
- (2) CHILDS, E. C. 1943 The water-table, equipotentials and streamlines in drained land. *Soil Sci.* 56: 317-330.
- (3) CHILDS, E. C. 1945 The water-table, equipotentials and streamlines in drained land: II. *Soil Sci.* 59: 313-327.

- (4) CHRISTENSEN, H. R. 1944 Permeability-capillary potential curves for three prairie soils. *Soil Sci.* 57: 381-390.
- (5) FAIR, G. M., AND HATCH, L. P. 1933 Fundamental factors governing the streamline flow of water through sand. *Jour. Amer. Waterworks Assoc.* 25: 1551-1565.
- (6) HATCH, L. P. 1940 Flow through granular media. *Jour. Appl. Mech.* 62: A109-112.
- (7) KOZENY, J. 1927 Über kapillare Leitung des Wassers im Boden. *Ber. Wien. Akad.* 136 A: 271-306.
- (8) RICHARDS, L. A. 1931 Capillary conduction of liquids through porous mediums. *Physics* 1: 318-333.
- (9) WILSON, B. D., AND RICHARDS, S. J. 1938 Capillary conductivity of peat soils at different tensions. *Jour. Amer. Soc. Agron.* 30: 583-588.



Mont Francis Morgan
1895-1945

Mont Francis Morgan

1895-1945

Agricultural science has sustained another of the casualties of war in the loss of Mont Francis Morgan, killed by enemy action on Leyte Island in the Philippines, where he was serving as a lieutenant colonel in the United States Army. Only meager details concerning his death are available, but we know that he was killed on January 15, 1945, when the Japanese attacked from ambush while he was leading a convoy of supplies for his unit. He was buried in the 77th Division Cemetery in Ormoc on Leyte.

An eminent soil scientist, Dr. Morgan had also a distinguished military career. In the First World War, during which he served as a company commander in France and in the Army of Occupation, he was decorated for bravery in action with both the Distinguished Service Cross and the Croix de Guerre. A reserve officer since the First World War, he re-entered active service in March, 1942, and was stationed in camps in the South until assigned to duty in the Pacific in November, 1944.

Between these two world wars that have so bitterly wasted so much of the genius and energy of his generation, M. F. Morgan succeeded not only in equipping himself with knowledge of a basic agricultural science but also in greatly advancing that science. His contributions achieved for him a national eminence in soil science, and they suggest the losses that soil science must sustain in his sacrifice.

He was 49 years old at the time of his death. Born on September 28, 1895, in New Martinsville, West Virginia, he attended the schools of that state and was graduated from the University of West Virginia in 1920, with a bachelor of science degree in agriculture. He was an instructor in soil science at that university in 1920 and 1921. In 1922 and 1923 he was assistant professor of agronomy at Ohio State University, where he obtained the degree master of science in 1922 and, in 1935, the degree doctor of philosophy.

Dr. Morgan's entire subsequent career was in association with the Connecticut Agricultural Experiment Station, his work there giving him an influence throughout the United States and in other countries also. He went to the Connecticut Station in 1923, to organize a department for the study of soils and soil use, and later was appointed chief agronomist of the station. His first undertaking was a revision and completion of the Connecticut Soil Survey, out of which developed his contributions on land classification and land use. He early made use of aerial photographs in soil and cover mapping. He set a pattern for other workers in his laboratory and field studies of Connecticut soils. He designed a method of soil testing that is now used in many parts of this country and abroad. He did notable work also on maintenance of soil organic matter, on fertilizer requirements of vegetables, and on simplifying the commercial grades of fertilizers. At the request of the United Fruit Company he made two trips to Central America

to study soil conditions relative to banana production. From 1927 to 1933 he held the rank of associate research professor in forest soils at the Yale School of Forestry. In July, 1941, he became a consulting editor of *SOIL SCIENCE*. In fact, Dr. Morgan had acquired such a broad knowledge and reputation that his advice was sought and his influence felt in connection with the solution of many problems relating to soil fertility, soil classification, and land use.

He was active in many scientific organizations. In 1933 he was president of the American Soil Survey Association, predecessor of the present Soil Science Society of America. In 1935 he was a member of the committee on arrangements for all American soil scientists attending the Third International Congress of Soil Science at Oxford, England. From 1936 until he re-entered military service he was secretary of the Section on Agriculture of the American Association for the Advancement of Science. He was a member of the American Society of Agronomy, the International Society of Soil Science, and the honorary scientific society Sigma Xi.

Fortunately a great deal of Dr. Morgan's work has become a permanent part of the literature of soil science. In addition to four circulars and to two bulletins written with co-workers, six bulletins by Dr. Morgan were published by the Connecticut Agricultural Experiment Station: "The Soils of Connecticut," "Microchemical Soil Tests," "The Universal Soil Testing System," "A Lysimeter Study of Soil Changes Resulting from Nitrogenous Fertilization," "The Soil Characteristics of Connecticut Land Types," and "Chemical Soil Diagnosis by the Universal Soil Testing System."

As senior author with J. H. Gourley and J. K. Ableiter, Dr. Morgan contributed to the U. S. Department of Agriculture's 1938 Yearbook *Soils and Men* the chapter on "The Soil Requirements of Economic Plants."

Other scientific contributions by Dr. Morgan include papers in *SOIL SCIENCE*, *Journal of Agricultural Research*, *Bulletin of the American Soil Survey Association*, *Transactions of the Third International Congress of Soil Science*, *Proceedings of the Soil Science Society of America*, *Journal of the American Society of Agronomy*, *American Potato Journal*, and *American Fertilizer*. He also reported on soil fertility experiments with vegetable crops in several issues of proceedings and reports of the Connecticut Vegetable Growers' Association.

His writings remain, and his example will long continue to influence the scientists and students with whom he worked, yet we have all lost greatly in his death—both personally and professionally. Those who knew Dr. Morgan well, admired his tremendous capacity for work and his ability to focus attention on main objectives while trusting details to others. His co-workers can testify that he was always readily approachable, never too busy to listen, ever ready to be helpful. He commanded respect and won esteem. In his death we all share a sacrifice of war, and as soil scientists we are left with a challenge to make as best we can the progress that might have been made more surely had he lived.

ROBERT M. SALTER.

STUDIES ON SOLONETZ SOILS OF ALBERTA¹

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The presence of soils with solonetz morphology has been reported in the United States and Canada by several investigators. Solonetzic soils are characterized by the development of a relatively impervious, strongly columnar B₁ horizon. This profile development has usually been attributed to the presence of relatively large proportions of sodium at some time, though such concentrations may no longer be present. These soils are most often found in regions where salts sufficient to warrant terming the soil "alkali" still occur. The presence of alkali in soils was observed and methods of reclaiming such areas were studied long before scientists were able to account for the origin of these soils. It was not until 1894 that the presence of columnar horizons in alkali soils was first pointed out by Zemiatchensky. This phenomenon of the soil profile has now been observed in many parts of the world, especially in the drier regions.

Hilgard defined alkali soils as those containing excessive amounts of soluble salts of continental origin. At the present time considerable difference of opinion still exists as to the evolution of alkali soils. In general, theories of Russian investigators as to the origin of these soils have been followed to a great degree. Gedroiz postulated that relatively large proportions of sodium in the soil were necessary to evolve the columnar structure and physical properties now present. De'Sigmond (20) concluded from his investigations that the factors responsible for the formations of alkali soils were: an arid or semiarid climate; an impervious subsoil or hard-pan layer; and a temporary abundance of humidity in the soil, interspersed with dry periods.

In English-speaking countries the term "alkali soil" generally means saline soil, the salts of which may be the sulfates, chlorides, carbonates, or nitrates of such bases as sodium, magnesium, and calcium. Russian scientists felt the need of a more specific term and divided alkali soils into three main groups, as follows: "solonchak" soils--saline soils which contain an abundance of soluble salts; "solonetz" soils--alkaline soils which contain relatively much replaceable sodium; and "sodol" soils--soils which were formerly solonetzic, but in which the exchangeable sodium has now largely been removed and exchangeable hydrogen substituted.

The origin and evolution of these soils have been outlined by Nikiforoff.³ The same author has said that besides the typical solonetz, there is a great group

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³ Nikiforoff, C. C. Evaluation of the alkali soils; their classification and reclamation. [Unpublished manuscript reported by Kellogg (12).]

of soils alkalized to a lesser degree. The chemical feature of these soils is the presence of exchangeable sodium, but in relatively small proportions. The physical and morphological feature is the compactness of the solonized section of the profile. The soils possess all the properties of the solonetz but to a lesser degree. Such soils are more common than the typical solonetz. Kellogg (12) points out that the most common occurrence of the solonchak, solonetz, and solod is as a complex, and within such an area profiles are present in intermediate stages of development.

Fieger and Sturgis (5) have reported a weak solonetz development artificially induced in the coastal prairie soils of Louisiana. Carpenter and Storie (3), Storie (21), and Kelley (11) have reported solonetz soils in California. Much work has been done in the various phases of these intrazonal soils in the Great Plains region. Murphy and Daniel (14) have compared the erodability of these soils with that of normal soils in Oklahoma. Kellogg (12) studied the occurrence of these soils in western North Dakota. Rost and his associates (17, 18, 19) have published several papers on the solonchak, solonetz, and solod soils of the Minnesota portion of the basin formed by glacial Lake Agassiz. Ellis and Caldwell (4) investigated similar soils in Manitoba, and Mitchell and Riecken (13) have reported on solonetz soils occurring in the brown and in the black soil zones of Saskatchewan. The last three groups of investigators have concurred in the finding that, if magnesium is not the dominant ion in the exchange complex of the A horizon, it rapidly becomes so with increasing depth. This chemical characteristic is probably not present in all intrazonal soils of this type.

The presence of eroded spots which are variously termed "slick spots," "blow-outs," or "burn-outs" appears to be a characteristic feature of at least some of the areas reported. The present investigation is a study of these intrazonal soils found in the brown and in the black soil zones of Alberta.

OCCURRENCE OF SOLONETZ SOILS IN ALBERTA

The four main soil zones of Alberta have been reported by Wyatt and Newton (23). The brown soils of the more arid southeast portion have developed under a mean annual precipitation of 10 to 14 inches. The black soils which developed to the north and west receive from 14 to 19 inches of precipitation each year.

The larger proportion of Alberta soils are glacial in origin. However, in the southeast portion of the province in which the brown soils are found, the present deposition of glacial till is, for the most part, relatively thin, the parent shales and sandstones of cretaceous origin being exposed in many places. In this case it is difficult to state definitely the origin of these soils, but it is reasonable to assume that at least a portion of the soils might be correctly designated as residual in nature.

A relatively large area in the brown soil region is composed of slightly alkaline soils. The presence of eroded and irregular shallow pit-like depressions, usually several feet across, is the most notable feature of the more level areas of this region. In some areas, the A horizon is essentially nonexistent. The general

appearance of this region corresponds to the description of the intrazonal soil areas in Saskatchewan and in North Dakota. The solonized brown soils of Alberta are in all probability only a portion of a very large region of intrazonal soils.

These intrazonal soils formed within the black zone are somewhat less spectacular than are the "slick spots" of the brown soil zone. Whereas the latter are often devoid of vegetation and present a washed, white, shiny appearance, the eroded spots occurring in the solonized black soils usually have a sparse growth of grass upon them which renders them less conspicuous. The characteristic "round-tops" of the B₁ horizon can be readily found, however, in the black soil zone and in the wooded soil zone as well as under the drier conditions.

MORPHOLOGY OF THE SOLONIZED PROFILE

The profile of the solonized brown soils varies considerably. The A horizon, often missing entirely, may be as much as 8 inches in thickness. The A₂ varies in thickness from a mere film to 2 or 3 inches and is of a gray-ash consistence and color, evidently being strongly leached. The highly colloidal B₁ horizon is strongly columnar, relatively impermeable, deflocculated, and dark brown in color. The upper surfaces in these columns are usually well developed, their biscuit-like appearance, when seen from above, justifying the expressive term "round-tops." Where the A horizon is missing, the crevices between these columns have been filled with a highly dispersed colloidal clay, resulting in a smooth washed clay surface. The entire upper B horizon is extremely colloidal and resistant to water penetration. The lower B horizons differ little in structure from corresponding horizons in normal soil profiles, though the nature and the concentration of the salts present are not necessarily the same.

The solonized profiles developed in the more humid black soil zone are generally characterized by deeper horizons. The black friable A₁ horizon varies from 2 to 20 inches in depth. The light-colored, leached A₂ horizon varies in thickness from a mere film covering the top of the B₁ horizon to that of a well-developed horizon with a thickness of 2 or 3 inches. Here it is more noticeable than in the brown soil zone. The B₁ horizon in the solonized horizon of the black soils is often waxy in appearance. As mentioned previously, the characteristic "round-tops" are often present in the solonized black soils and also in the solonized podzolic soils. The B₂ horizon is encountered at greater depths in the black and wooded soils than in the brown soils.

EXPERIMENTAL METHODS

Water-soluble bases

Duplicate 10-gm. samples of air-dry soil were placed in a constant level leaching apparatus and slowly extracted with 500 ml. of CO₂-free distilled water. The leachate was evaporated to a low volume, filtered, washed with hot water, and made up to volume. Soluble calcium, magnesium, sodium, and sulfate were determined on aliquots of this solution.

Exchangeable bases

After the leaching with water, the same soil samples were leached with 750 ml. of normal ammonium acetate adjusted to a pH of 6.9. This leachate was evaporated to dryness to dehydrate any silica, treated with concentrated nitric acid, and again evaporated to dryness. A few milliliters of concentrated hydrochloric acid was then added and the leachate evaporated to dryness before the residue was taken up with a few milliliters of hydrochloric acid, filtered, washed with hot water, and made up to volume. Exchange calcium, magnesium, sodium, and the sulfate were determined on aliquots of this solution.

Base-exchange capacity

After being leached with water and then with ammonium acetate, the duplicate soil samples were immediately saturated with calcium by leaching with 750 ml. of normal calcium chloride. The excess calcium not held by the exchange complex was then removed by leaching with distilled water until the leachate gave no further test for calcium. The soil was then leached with 750 ml. of normal ammonium acetate solution, and this leachate treated in a manner similar to that of the exchange leachate, but analyzed for calcium only. The number of milligram equivalents per 100 gm. of air-dry soil was considered to be a measure of the total exchange capacity.

Calcium was determined by precipitation as the oxalate and titration with 0.05 N KMnO_4 .

Magnesium was determined on the calcium filtrate by precipitation with $\text{NaNH}_2\text{HPO}_4$ solution, filtered, the precipitate dried, dissolved in standard acid, and titrated with a standard base.

The sodium was determined gravimetrically according to the method of Barber and Kolthoff (1).

Sulfates were determined gravimetrically by precipitation as the barium salt, filtered, washed, and ignited in a muffle furnace at 700°C .

Potassium was not determined.

RESULTS

Several phases of the problem were studied. Eighteen profiles from the brown soil zone were analyzed. Of these, thirteen were solonized to varying degrees, and the remaining five were normal (nonsolonized) profiles. Nine profiles from the black soil zone are reported. Of these, six were solonized, and the remainder, which were sampled immediately adjacent to the solonized area, were apparently normal in structure. It is obviously impractical to report on individual profiles, and some variability might be eliminated if the data from profiles having much the same morphology are presented in the form of the mean value together with the extreme variation of the bases present. In many of the soil profiles it was not practical to sample the C horizon, and therefore this horizon is not included in any of the averages (see footnote table 3).

The first problem was to determine whether the so-called solonetz soils of Alberta are similar in exchange-base content to those reported from other parts

of the world. Many investigators have found that if high concentrations of exchange sodium were present at one stage of development in these intrazonal soils, this ion is not dominant in the exchange complex at the present time. Several of these workers have reported magnesium to be the dominant exchange ion now present in the B_1 horizon, this feature becoming more accentuated in the lower horizons. Rost (17) compared profiles in which several investigators found exchange magnesium of the B horizons in maximum and minimum proportions of the exchange bases present. His results, extended to include more recent studies on the subject, are presented in table 1.

The solonized soils of Oklahoma reported by Murphy and Daniel are highest in the proportions of exchange sodium. The B_1 horizons of the North Dakota solonized profiles are not of necessity dominated by the exchange magnesium. The proportions of exchange magnesium reportedly found in California, Minnesota, and Saskatchewan soils, however, appear possibly to justify the term "magnesium solonetz." The Saskatchewan investigators reported on one typically solonized profile from each of two soil zones. It should not be assumed that all of the solonetzic soils of Saskatchewan would of necessity be dominated by magnesium in the exchange complex.

The maximum percentages of exchange magnesium in the B_1 horizon of the solonized Alberta soils are not sufficiently high to warrant a statement that this horizon is dominated by exchange magnesium. It will be shown subsequently that calcium is in general the dominant exchange ion present throughout the entire profile. The present investigation did not include the determination of potassium, but it is known that the exchange potassium of these soils is low, and its omission should not seriously affect the percentage exchange-base balance.

Some question existed as to possible differences in the content and proportion of bases in solonized profiles of the black soil zone and in profiles developed under the drier conditions of the brown soil zone. Table 2 gives the average milligram equivalents and average relative proportions of water-soluble, exchangeable, and total bases found in six such profiles from the black soil zone and in thirteen profiles from the brown soil zone.

The amounts of water-soluble calcium and magnesium in the solonized profiles from the two soil-zones are much the same, with larger amounts of calcium being present in the B_2 horizons of the black soils. Since both the amount and the proportion of sodium in the solonized profiles of the black soil zone are higher, however, than in the profiles from the brown zone, the water-soluble calcium and magnesium in the brown soils are relatively more dominant.

Calcium is the dominant exchange ion in solonized profiles from both soil zones, though the amounts of this ion in the B_2 horizon are erroneously high because of errors produced by solubility effects in the extraction process. The content and proportion of exchange magnesium is intermediate between the calcium and sodium and though the amount of magnesium in general increases with depth, there is no consistent increase in the proportion of this ion. The proportions of magnesium and sodium in the B_2 horizons probably would be higher if soluble calcium materials in the soil had not been attacked by the

leaching agent. The amounts and proportions of exchange sodium in the black soil zone profiles are consistently greater than in the horizons of the brown soils.

TABLE 1

Maximum and minimum amounts of exchangeable magnesium reported present in the B₁ horizon of solonetz and solonetz-like soils of the United States and Canada

DESCRIPTION	REPORTED BY	PERCENTAGE OF TOTAL BASES				
		Mg	Ca	Na	K	Na + K
California						
San Luis Obispo	Kelley	66	27	6	1	
Pasa Robles	Kelley	40	49	10	1	
North Dakota						
Profile 11*	Kellogg	47	39	12	2	
Profile 9	Kellogg	24	64	10	2	
Oklahoma						
Stillwater farm A†.	Murphy and Daniel	27	32	37	4	
Stillwater farm E	Murphy and Daniel	15	24	56	5	
Minnesota						
Profile 4	Rost	76	19	4	1	
Profile 6	Rost	58	38	2	2	
Saskatchewan						
Profile 2*	Brown soils Mitchell and Riecken	72	19	*	.	9
Profile 6*	Black soils Mitchell and Riecken	77	17	..		6
Alberta						
Maximum Mg in 13 analyzed profiles	Brown soils MacGregor and Wyatt	57	27	16	..	
Minimum Mg in 13 analyzed profiles	MacGregor and Wyatt	26	60	14	.	
Maximum Mg in 6 analyzed profiles	Black soils MacGregor and Wyatt	42	27	31	—	
Minimum Mg in 6 analyzed profiles	MacGregor and Wyatt	10	89	1	—	

* Calculated from the sum of exchangeable Ca, Mg, Na, and K.

† 1- to 12-inch section of exposed B horizon.

This feature might be expected with the larger amounts of water-soluble sodium of the black soils.

For simplicity, the average exchange capacity and the average amount of exchange hydrogen present in these profiles are not shown. It may be noted, however, that the total exchange capacity of the black soil profiles is consistently higher than that of the brown soils. The black soils may contain a measurable amount of exchange hydrogen in the A horizons, and in some cases this feature may also be present in the B₁ horizon. The brown soils usually do not contain measurable quantities of exchange hydrogen, although a few of the profiles analyzed were thought possibly to contain some hydrogen in this form. The heavier precipitation and the lower evaporation rate under which the black soils

TABLE 2

Comparison of milligram equivalents and percentages of water-soluble, exchangeable, and total bases present in 13 solonized brown soil zone profiles and 6 solonized black soil zone profiles

HORIZON	MILLIGRAM EQUIVALENTS PRESENT						PERCENTAGE OF BASES PRESENT					
	Average of 13 solonized profiles brown soil zone			Average of 6 solonized profiles black soil zone			Average of 13 solonized profiles brown soil zone			Average of 6 solonized profiles black soil zone		
	Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na
<i>Water-soluble bases</i>												
A ₁	0.5	0.3	0.4	0.5	1.0	1.5	42	25	33	17	33	50
A ₂	0.6	0.4	0.5	0.4	0.8	0.9	40	27	33	19	38	43
B ₁	0.6	0.5	1.4	0.9	1.0	3.3	24	20	56	17	19	64
B ₂	3.1	1.4	2.4	6.3	1.4	4.7	45	20	35	51	11	38
<i>Exchangeable bases</i>												
A ₁	7.1	3.2	0.4	15.0	6.1	1.6	66	30	4	66	27	7
A ₂	6.0	2.8	0.4	9.4	4.8	0.8	65	31	4	63	32	5
B ₁	13.7	9.1	1.6	25.4	9.4	4.6	56	37	7	64	24	12
B ₂	56.1	9.0	0.8	59.8	9.7	1.0	85	14	1	85	14	1
<i>Total bases</i>												
A ₁	7.6	3.5	0.8	15.5	7.1	3.1	64	29	7	60	28	12
A ₂	6.6	3.2	0.9	9.8	5.6	1.7	62	30	8	57	33	10
B ₁	14.3	9.6	3.0	26.3	10.4	7.9	53	36	11	59	23	18
B ₂	59.2	10.4	3.2	66.1	11.1	5.7	81	14	4	80	13	7

have developed probably explain any unsaturation of these soils. These factors also may have brought about the higher sodium content of the solonized black soils by aiding in the solution and transfer of this ion from the normal soils to the lower-lying solonized areas.

There has been considerable speculation as to why the A horizon of solonized soils has eroded only in irregular patches and has not eroded from adjacent land, which, except for the presence of the A horizon, is apparently the same. Several of these eroded profiles in the brown soil zone were examined and compared structurally with profiles developed 4 to 50 feet from the eroded spot on much the same surface level. In some cases the profiles examined at the middle and

at the edge of the eroded spot were almost identical in morphological development to noneroded profiles occurring at distances varying up to 50 feet. In other cases it was observed that the noneroded profiles showed slightly less structural development of the B₁ horizon. These differences, however, were not great.

TABLE 3

Range and average and milligram equivalents and percentages of water-soluble, exchangeable, and total bases present in solonized profiles of the brown soil zone

Averages of six eroded or near-eroded profiles and of six profiles 4 to 50 feet from erosion

HORIZON	MILLIGRAM EQUIVALENTS PRESENT								PERCENTAGE OF BASES PRESENT*							
	Number of horizons in average	Average of eroded or near-eroded profiles			Number of horizons in average	Average of profiles 4-50 feet from erosion			Average of eroded or near-eroded profiles			Average of profiles 4-50 feet from erosion				
		Ca	Mg	Na		Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na		
Water-soluble bases																
Average																
A ₁	4	0.4	0.3	0.6	6	0.5	0.3	0.3	31	23	46	46	27	27		
A ₂	3	0.6	0.3	0.6	4	0.7	0.5	0.3	40	20	40	47	33	20		
B ₁	6	0.6	0.6	2.0	6	0.7	0.5	0.7	19	19	62	37	26	37		
B ₂	6	4.7	1.9	3.9	6	1.9	1.0	1.0	45	18	37	48	26	26		
Range																
A ₁	4	0.2-0.7	0.2-0.4	0.4-0.7	6	0.3-0.7	0.2-0.8	0.2-0.4	25-40	13-27	31-54	40-54	20-47	12-40		
A ₂	3	0.2-1.1	0.2-0.4	0.2-1.0	4	0.2-1.1	0.2-0.8	0.2-0.4	22-50	16-33	17-56	33-50	29-36	14-33		
B ₁	6	0.4-1.1	0.3-1.0	0.3-3.5	6	0.2-1.7	0.1-0.9	0.3-1.1	10-46	8-31	23-70	29-47	17-42	24-58		
B ₂	6	0.4-18.4	0.2-6.8	0.8-8.3	6	0.2-3.0	0.1-1.7	0.3-1.6	10-55	4-40	15-74	32-58	16-32	11-50		
Exchangeable bases																
Average																
A ₁	4	7.0	3.2	0.5	6	6.9	3.4	0.4	65	30	5	64	32	4		
A ₂	3	4.9	2.3	0.4	4	6.9	3.4	0.4	65	30	5	64	32	4		
B ₁	6	12.8	10.4	2.4	6	17.5	8.4	0.5	50	40	10	66	32	2		
B ₂	6	67.3	9.5	0.8	6	51.7	8.9	0.4	87	12	1	84	15	1		
Range																
A ₁	4	3.8-10.7	1.3-4.4	0.4-0.6	6	6.5-8.9	2.1-4.5	0.3-0.5	62-69	23-35	3-10	63-74	21-34	3-5		
A ₂	3	2.5-5.9	1.0-4.0	0.3-0.6	4	5.0-9.2	1.7-4.5	0.3-0.5	57-74	22-39	4-15	60-69	24-37	3-7		
B ₁	6	3.6-20.5	7.7-14.6	0.4-4.0	6	8.3-30.5	3.4-11.0	0.4-0.6	27-64	33-57	2-17	60-73	26-43	1-4		
B ₂	6	11.1-109.0	3.2-17.0	0.6-1.2	6	5.8-87.0	2.6-13.8	0.4-0.6	73-95	4-21	1-6	58-89	10-40	1-7		
Total bases																
Average																
A ₁	4	7.4	3.5	1.1	6	7.4	3.7	0.7	62	29	9	63	31	6		
A ₂	3	5.5	2.6	1.0	4	7.6	3.9	0.7	60	29	11	62	32	6		
B ₁	6	13.4	11.0	4.4	6	18.2	8.9	1.2	47	38	15	65	31	4		
B ₂	6	72.0	11.4	4.7	6	53.6	9.9	1.4	82	13	5	83	15	2		
Range																
A ₁	4	4.0-11.1	1.5-4.7	1.0-1.1	6	7.2-9.4	2.3-5.1	0.6-0.7	58-66	23-34	8-15	60-72	21-36	4-7		
A ₂	3	2.7-7.4	1.2-4.4	0.6-1.3	4	5.2-9.9	1.9-5.3	0.6-0.7	54-67	21-38	5-22	59-67	24-37	5-9		
B ₁	6	4.0-21.0	8.3-15.3	3.3-6.4	6	8.7-32.2	3.5-11.9	0.8-1.7	26-66	30-53	3-21	54-71	26-43	3-6		
B ₂	6	11.5-111.1	3.8-19.2	1.4-9.0	6	6.0-89.4	2.7-15.3	0.9-2.0	60-92	5-20	1-20	63-88	10-39	1-9		

* In some instances the average percentage of bases (especially Na) is reported as equal to the minimum range. This seeming error is introduced by the variations of Ca, Mg, and Na contents in the individual profiles not reported as such.

The average analyses for each horizon of six profiles taken from the center or the sides of eroded spots were compared to averages from an equal number of profiles which were selected up to 50 feet from the sampled "slick spots" of the area. These comparative samples were taken at random over the entire solonized area of the brown soil zone. Table 3 gives the mean range, average, and

proportional importance of water-soluble, exchange, and total calcium, magnesium, and sodium of the eroded and adjacent noneroded soil profiles. The number of horizons averaged in each case is given, since some horizons were necessarily absent in some of the profiles.

The main difference in the soluble-base content of the eroded and noneroded profiles is the higher quantity and proportion of soluble sodium found in the eroded profiles. Soluble calcium and magnesium averaged approximately the same, soluble salts being much more abundant in the B₂ horizon of the eroded profiles. This increase is probably largely brought about by the more impervious nature of the B₁ horizon in the eroded profiles.

Calcium is the dominant exchange base in both profile groups. As might be expected from the soluble-base concentration, the amount and proportion of exchange sodium is slightly higher in the six eroded profiles than in the noneroded, this difference being marked in the B₁ horizon. The proportionate differences in the amounts and percentages of total sodium present, with little difference in the divalent ion content of the two groups, seems to indicate that the differences in the sodium content is the only clue in this study as to why the erosion of the A horizons occurred. There is no significant difference in the base saturation of these two groups of profiles, since all profiles were essentially base-saturated.

In the profiles analyzed, only traces of soluble sulfate were present in the A₁, A₂, and B₁ horizons. Only three B₂ horizons of the nineteen profiles studied in the brown soil zone contained soluble sulfates in sufficient quantities to be determined by the common macrochemical methods, all three of these being solonized and eroded profiles. The B₂ horizons of these profiles contained 1,070, 1,390, and 19,190 p.p.m. of sulfate. This would suggest that the soluble bases present in the three upper horizons were at least partly in some other combination than as the sulfate, whereas in the B₂ horizons considerable amounts of sulfate salts do occur in at least some of the eroded profiles.

A possible explanation of the larger amounts of sodium found in the B₁ horizons of the eroded profiles is that the washed, deflocculated remnants of the A₂ horizon are effective in preventing the actual penetration of water through the upper surface of the B₁ horizon. The water which collects in the "slick spot" probably brings in some sodium as it migrates through the A horizons of the surrounding noneroded soils. This salt-bearing water becomes trapped on the "slick spot" surface, and the sodium of the deflocculated A₂ horizon is further increased as the water evaporates. If this does occur, the soluble and exchange sodium now present in the eroded complex B₁ horizons is in all probability of ancient origin and exhibits little or no mobility. Possibly this feature of higher sodium content of the deflocculated B₁ horizon of the eroded profiles is the only remaining indication of a period in which the sodium content of the soil was much higher than it is now.

Solonized soils are commonly found on the level to undulating areas of the brown soil zone. They are, however, sometimes found on the upper slopes of local elevations. The areas of solonized soils are also bounded by level to un-

dulating normal soils which have apparently developed under much the same climate, topography, and vegetation. The presence of normal profiles on the higher elevations of the solonized area would suggest difference in drainage conditions, whereas the normal soil development of soils on topography in which

TABLE 4

Range and average of milligram equivalents and percentages of water-soluble, exchangeable, and total bases present in thirteen solonized and five nonsolonized (normal) brown soil profiles

HORIZON	MILLIGRAM EQUIVALENTS PRESENT								PERCENTAGES OF BASES PRESENT*					
	Number of horizons in average	Average of 13 solonized profiles			Number of horizons in average	Average of 5 normal profiles			Average of 13 solonized profiles			Average of 5 normal profiles		
		Ca	Mg	Na		Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na
Water-soluble bases														
Average														
A ₁	11	0.5	0.3	0.4	5	0.8	0.4	0.2	42	25	33	57	29	14
A ₂	8	0.6	0.4	0.5	3	0.8	0.4	0.3	40	27	33	53	27	20
B ₁	13	0.6	0.5	1.4	5	0.7	0.3	0.3	24	20	56	54	23	23
A ₂	13	3.1	1.4	2.4	5	1.1	0.7	0.6	45	20	35	46	29	25
Range														
A ₁	11	0.2-0.7	0.2-0.8	0.2-0.7	5	0.7-1.0	0.2-0.8	0.2-0.2	25-54	13-47	12-54	41-64	18-47	12-18
A ₂	8	0.2-1.1	0.2-0.8	0.2-1.0	3	0.6-1.1	0.2-0.8	0.2-0.3	22-50	15-36	14-56	50-64	18-36	14-27
B ₁	13	0.4-1.7	0.1-1.0	0.3-3.5	5	0.4-1.0	0.1-0.7	0.2-0.5	10-47	8-42	23-70	29-66	12-42	12-38
B ₂	13	0.4-18.4	0.1-6.8	0.3-8.3	5	0.4-2.1	0.2-1.2	0.3-1.4	10-58	4-40	11-74	32-64	18-33	8-36
Exchangeable bases														
Average														
A ₁	11	7.1	3.2	0.4	5	12.6	4.4	0.4	66	30		72		
A ₂	8	6.0	2.8	0.4	3	9.1	4.2	0.3	65	31		67		
B ₁	13	13.7	9.1	1.6	5	12.2	5.9	0.3	56	37		66		
B ₂	13	56.1	9.0	0.8	5	38.1	8.9	0.4	85	14		80		
Range														
A ₁	11	3.8-10.7	1.3-4.5	0.4-0.6	5	7.9-15.7	4.0-5.1	0.3-0.4	62-76	21-35	3-10	63-74	22-34	2-2
A ₂	8	2.5-9.2	1.0-4.5	0.3-0.6	3	7.2-11.2	3.8-4.5	0.3-0.3	57-74	20-39	3-16	60-70	28-37	2-3
B ₁	13	3.6-30.5	3.4-14.6	0.4-4.0	5	7.6-16.8	3.5-6.9	0.3-0.4	27-73	26-57	1-16	67-72	27-38	1-2
B ₂	13	5.8-109.0	2.6-17.0	0.4-1.2	5	8.9-90.4	4.6-15.0	0.3-0.5	58-95	4-40	1-13	58-85	14-40	1-2
Total bases														
Average														
A ₁	11	7.6	3.5	0.8	5	13.4	4.8	0.6	64	29	7	71	26	3
A ₂	8	6.6	3.2	0.9	3	9.9	4.6	0.6	62	30	8	65	31	4
B ₁	13	14.3	9.6	3.0	5	12.9	6.2	0.6	53	36	11	65	32	3
B ₂	13	59.2	10.4	3.2	5	39.2	9.6	1.0	81	14	5	79	19	2
Range														
A ₁	11	4.0-11.1	1.5-5.1	0.6-1.1	5	8.6-16.6	4.2-5.4	0.5-0.6	58-73	20-36	4-15	60-75	22-36	3-4
A ₂	8	2.7-9.9	1.2-5.3	0.6-2.2	3	8.3-11.8	4.0-5.3	0.5-0.6	54-67	21-38	5-22	59-69	27-37	4-4
B ₁	13	4.0-32.2	3.5-15.3	0.8-6.4	5	8.0-17.6	3.6-7.3	0.5-0.9	26-71	25-53	3-21	57-72	26-38	2-5
B ₂	13	6.0-111.1	2.7-19.2	0.9-9.0	5	9.3-92.6	4.8-16.2	0.6-1.9	57-92	5-39	1-20	55-84	15-39	1-6

* See footnote table 3.

solonization usually occurs would suggest possible differences in parent material. This question was studied to determine whether significant differences in the base content and proportion of bases occurred in the solonized and nonsolonized soils of the same general area. Two normal profiles from the central part and three from the northern edge of the solonized area were obtained. The average and the range of bases in these five normal profiles are compared, in table 4,

with averages obtained from thirteen solonized profiles. The number of horizons averaged in each case is shown.

The average soluble and exchange sodium content of the thirteen solonized profiles is significantly greater than that of the five normal profiles. The proportion of sodium to the divalent bases of the two groups is of the same order. Calcium is the dominant exchange base, this being more marked in the normal soil profiles. The magnesium content and proportion of these two groups of soils are much the same, with the solonized profiles simply having sodium in place of the higher proportions of calcium. Since the exchange complex of these soils is usually in the saturated state, the exchange capacity of the normal soils is higher than that of the solonized profiles. This increased capacity is mainly occupied by the divalent ions. The effect of a high divalent-monovalent ratio is well known and probably plays an important rôle in the development of these normal soils under much the same climate as that under which the solonized profiles were developed. As previously mentioned, soluble sulfate in appreciable quantities occurs in the B₂ horizons of some of the solonized soils, whereas only traces occur in the same horizon of normal soil profiles.

The solonized areas in the black soil zone have already been mentioned and some of their characteristics discussed. It was desirable to determine the difference, if any, between these solonized soils and morphologically normal soil profiles which were developed but a few rods distant. Three of these so-called "normal" profiles immediately adjacent to the solonized area were selected. The A horizon of the "normal" profiles showed no natural division, which made it impractical to obtain a definite A₂ horizon. Table 5 compares the average base content and range of the six solonized profiles with average analyses of the three normal profiles.

The amounts and proportions of the soluble and exchangeable divalent bases of both solonized and normal profile groups are extremely variable. The larger quantities of both soluble and exchangeable sodium in all horizons of the solonized profiles are consistent and probably are significant. Exchangeable hydrogen was present in the A₁ horizon of five of the six solonized profiles, the amounts ranging from 4.9 to 15.4 m.e., the average being 8.6 m.e. One of the two solonized A₂ horizons contained 2.8 m.e. of exchange hydrogen, and three of the six B₁ horizons were unsaturated, containing from 0.4 to 10.0 m.e. and averaging 4.7 m.e. of exchange hydrogen. In the adjacent normal soil profiles, 2.8 m.e. of exchange hydrogen was found only in one A horizon of the three profiles. Since potassium was not determined, probably some of these amounts of exchange hydrogen are not significant, but since the amount of exchange potassium is known to be low, it would seem that the solonized complex of the black soil zone probably contains larger amounts of exchange hydrogen in general than do the normal soils developed immediately adjacent to the solonized area.

As in the soils of the brown soil zone, the three upper horizons of the black soils contain soluble sulfates in trace amounts only. The B₂ horizons of the three normal black soils analyzed were likewise low in sulfate content, but in three of the six solonized profiles, measurable quantities of soluble sulfate were

found. The amounts present were 3,580, 4,920, and 15,740 p.p.m. respectively. These quantities would largely account for the great increase in the average amount of soluble calcium, magnesium, and sodium in the B₂ horizons of the

TABLE 5

Range and average of milligrams equivalents and percentages of water-soluble, exchangeable, and total bases present in six solonized profiles in the black soil zone in comparison with those present in three adjacent normal profiles

HORIZON	MILLIGRAM EQUIVALENTS PRESENT								PERCENTAGES OF BASES PRESENT*								
	Number of horizons in average	Average of six solonized profiles			Number of horizons in average	Average of three normal profiles adjacent to solonized area			Average of six solonized profiles			Average of three normal profiles adjacent to solonized area					
		Ca	Mg	Na		Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na			
Water-soluble bases																	
Average																	
A ₁	6	0.5	1.0	1.5	3	0.9	0.9	0.5	17	33	50	39	39	22			
A ₂	2	0.4	0.8	0.9	0				19	38	43						
B ₁	6	0.9	1.0	3.3	3	0.6	0.9	0.7	17	19	64	27	41	32			
B ₂	5	6.3	1.4	4.7	3	1.9	1.0	0.9	51	11	38	50	26	24			
Range																	
A ₁	6	0.3-1.2	0.8-1.0	0.4-2.2	3	0.7-1.1	0.8-0.9	0.3-1.0	9-46	26-39	15-65	36-48	29-47	13-35			
A ₂	2	0.2-0.6	0.6-0.9	0.6-1.1	0				9-34	33-41	33-50						
B ₁	6	0.5-1.2	0.7-1.3	0.8-6.2	3	0.5-0.7	0.7-1.0	0.3-1.7	13-30	14-36	35-73	21-34	28-57	12-51			
B ₂	5	1.1-21.4	0.8-1.9	1.0-8.9	3	1.8-2.0	0.9-1.2	0.3-2.0	4-77	7-23	12-81	39-58	19-35	7-42			
Exchangeable bases																	
Average																	
A ₁	6	15.0	6.1	1.6	3	32.3	8.5	0.4	66	27	7	78	21	1			
A ₂	2	9.4	4.8	0.8	0				63	32	5						
B ₁	6	25.4	9.4	4.6	3	21.3	9.5	0.8	64	24	12	67	30	3			
B ₂	5	59.8	9.7	1.0	3	62.1	13.0	0.3	85	14	1	82	17	1			
Range																	
A ₁	6	5.2-29.3	3.5-7.1	1.0-2.2	3	24.6-36.9	7.2-9.4	0.3-0.5	50-81	18-39	1-17	77-79	20-22	1-1			
A ₂	2	5.2-13.5	3.6-6.0	0.4-1.2	0				52-68	30-36	2-12						
B ₁	6	6.7-84.2	8.2-11.8	1.1-8.7	3	16.6-24.8	9.2-9.6	0.3-1.7	27-89	10-42	1-32	64-72	27-35	1-5			
B ₂	5	25.0-102.8	8.6-11.4	0.4-3.0	3	50.2-85.2	9.6-14.8	0.2-0.5	72-92	7-27	1-4	77-89	10-22	1-1			
Total bases																	
Average																	
A ₁	6	15.5	7.1	3.1	3	33.2	9.4	0.9	60	28	12	76	22	2			
A ₂	2	9.8	5.6	1.7	0				57	33	10						
B ₁	6	26.3	10.4	7.9	3	21.9	10.4	1.5	59	23	18	65	31	4			
B ₂	5	66.1	11.1	5.7	3	64.0	14.0	1.2	80	13	7	81	18	1			
Range																	
A ₁	6	5.5-30.5	4.5-8.3	0.9-4.1	3	25.7-37.6	8.1-10.8	0.6-1.4	42-78	20-37	2-24	75-77	21-23	1-3			
A ₂	2	5.4-14.1	4.5-6.6	1.0-2.2	0				45-65	30-37	5-18						
B ₁	6	7.8-85.3	9.2-12.5	1.4-11.8	3	17.2-25.3	10.2-10.5	0.5-3.4	26-83	10-39	7-35	62-70	28-36	2-9			
B ₂	5	6.21-124.2	10.0-13.3	1.5-11.9	3	42.0-87.0	10.5-16.0	0.5-2.5	73-89	7-26	2-15	77-87	11-23	1-2			

* See footnote table 3.

solonized black soils in comparison to the lower soluble base content of the three upper horizons.

DISCUSSION

The analysis of nineteen profiles of the so-called morphological solonetz soils of Alberta has shown that the average content and the proportion of exchange

sodium in relation to total exchange bases are low. In the B₁ horizons, the exchange sodium of thirteen solonized brown soil zone profiles averaged 7 per cent of the exchange bases present, whereas that of six solonized profiles of the black soil zone averaged 12 per cent. These figures do not agree with the classification of Gedroiz respecting solonized soils, but they are in harmony with the results of most of the investigations on this type of intrazonal soil on the North American continent. The following extreme proportional ranges of exchange sodium have been found in the B₁ horizons of soils in North America:

INVESTIGATOR	PLACE	NUMBER OF PROFILES	MINIMUM % Na	MAXIMUM % Na
Murphy and Daniel (14)	Oklahoma	23	22	58
MacGregor and Wyatt	Alberta (black)	6	1	32
Stalwick ⁴	Saskatchewan	5	7	22
Kelley (11)	California	7	5	18
MacGregor and Wyatt	Alberta (brown)	13	1	16
Rost (17)	Minnesota	6	2	6

The sodium soil class of de'Sigmond (20) requires a minimum of 12 per cent of the exchange sodium in the B₁ horizon. It would appear that, of the foregoing soils, the solonized soils of Oklahoma alone would entirely meet this qualification.

The Alberta soils investigated do not, in general, contain 12 per cent of exchange sodium. They are saturated chiefly with calcium and to a lesser degree with magnesium. The colloidal fraction is generally unstable because of the flocculation induced by the large proportion of divalent cations. The reaction of these soils for the most part falls within a 6.5 to 8.3 pH range. All of these features agree with the calcium soil order of de'Sigmond. In general it would seem that designating soil classes by any rigid proportion of ions in the solonized complex is not compatible with known soil variability.

Since the chemistry of most of the solonized areas on this continent at present are not entirely consistent with the Gedroiz theory of their genesis, many theories have been advanced to explain the formation of the highly colloidal impervious B₁ horizon in these soils. No investigator has as yet offered an explanation of such a profile development which entirely eliminates the Gedroiz sodium theory. Bray (2) considered that claypan formation was produced largely by the migration of fine clay particles from eluvial to illuvial horizons. He also considered that only slight unsaturation would allow the migration of the fine clay colloid. This would not explain the formation of a highly colloidal B₁ horizon in a solonized soil which is fully saturated at the present time unless the soil was unsaturated at one time. Recently Nikiforoff and Drosdoff (15) pointed out that a soil developing from a homogenous parent material develops individual characteristics in the different horizons which are due to certain

⁴ Stalwick, A. E. 1938 Comparative physical and chemical studies on some solonetz and non-solonetz soils of Saskatchewan, Canada. [Master's thesis, University of Saskatchewan, Saskatoon.]

changes in the original material and that the changes taking place in any horizon are different from those in other horizons. These changes probably are initiated by the decomposition of certain minerals, and further modification of the horizons depend considerably upon what happens to the products of the original mineral decomposition. Some changes are induced by the recombination of the original constituents with little or no movement, whereas other changes are largely dependent on the movement of various substances which have been freed to move by the original breakdown of the mineral. Modification of original soil materials present in any horizon is rarely brought about by either recombination or migration of ions alone.

Rost (17), Rost and Maehl (19), Ellis and Caldwell (4), Mitchell and Riecken (13), Riecken (16), and Kelley (11) found definite increases of replaceable magnesium in the lower horizons of the solonized profile, magnesium becoming the dominant exchange base in the illuvial horizons. Riecken (16) has formulated a theory as to this dominance of magnesium in the exchange complex, but does not assume that this element has occupied the rôle usually ascribed to sodium in the morphological and chemical development of solonetz. Kelley (10) points out the important point that magnesium clays are much more colloidal than calcium clays. Sushko (22) concludes that the amount of exchange magnesium present is correlated with the degree of solodization in the profile, but does not associate the presence of this base with the evolution of the profile.

Little such concentration or dominance of replaceable magnesium in the lower horizons of the Alberta solonetzic soils was observed in this study, calcium being the dominant base in nearly all cases. This dominance of exchange calcium, at least in the lower B horizons, may have been brought about to some extent by errors in the amount of exchange calcium determined, due to the presence of large amounts of carbonate in most of the B₂ horizons studied. The small amount of eluviation is about what would be expected in soils formed under such dry climatic conditions.

Jenny and Smith (8) consider that the presence of electrolytes favors the retention of colloidal material in the B horizon. The most striking feature of the solonized profiles found in Alberta is the columnar, compact, and essentially impervious B₁ horizon underlain by the highly calcareous B₂ horizon. Soluble sulfates appear to concentrate in this horizon beneath the eroded "slick spots" and may increase in concentration as the parent material is approached.

Rost and Maehl (19) have reported the presence of appreciable quantities of exchange hydrogen in solodized soils of the Red River valley. Mitchell and Riecken (13) point out that slight unsaturation of the A horizon is a common feature of the solonized soils of Saskatchewan. Under such conditions, eluviation of materials through the profile should be possible. The presence of exchange hydrogen was observed in the upper horizons of the Alberta black soil profiles, and was especially marked in several of the solonized samples. In the soils of the brown zone, no definite evidence of base unsaturation was observed, although small amounts of exchange hydrogen may have been present in the A₂ horizon of two of the solonized profiles. The method of determining exchange

hydrogen by difference was employed, but this is unsatisfactory, especially in the detection of small amounts. The amount of exchange hydrogen found in this study is small and agrees with the findings reported on normal soils of this region by Holowaychuk (7). Gammon *et al.* (6) found that ammonium acetate (which was used in this investigation) as an extractant tends to give erroneously high amounts of exchange hydrogen. If the Gedroiz theory of base saturation is true, the high concentrations of carbonates occurring relatively close to the soil surface in the brown soil zone would maintain a saturated exchange condition. The higher precipitation and lower evaporation rates of the black soil region should have favored the downward movement of electrolytes.

The presence of soluble sulfates in the B₂ horizons of the more markedly solonized profiles is evidently the result rather than a contributing factor in the solonization process. The relative absence of this anion in the illuvial horizons of the normal soils suggests that the impermeable B₁ horizons of the solonized soils have interfered with the normal downward movement of the sulfate.

The solonized soils of Alberta fall in the slightly alkaline soil group of Kelley and Brown (9). They do not contain sufficient sodium, however, to warrant inclusion in the Gedroiz classification as a sodium solonetz. De'Sigmond (20) included soils containing 12 to 15 per cent exchange sodium (of the exchange bases present) in his sodium soil class. Since the exchange sodium in the B₁ horizons of the black soils averaged 12 per cent, it might be possible to include some of the solonized black soils in this sodium class. The proportions of sodium in the solonized brown soils would be too low to warrant placement of the soils in the sodium grouping, but according to Glinka and de'Sigmond the soils would be classed as "solonetz-like." Since the solonized soils of the brown and black soils exhibit similar physical characters, though the black soils here studied contained proportionately more sodium, the separation of these soils on a purely chemical basis does not appear to be consistent. For simplicity, the morphological solonetz soils of Alberta included in the study could all be termed "solonetz-like."

SUMMARY

Studies on the base-exchange properties of solonized soils found in the brown and in the black soil zones of Alberta are reported. The exchange complex of nearly all of the profiles examined contained calcium as the dominant ion, magnesium being appreciably lower. The amount of sodium usually present in the exchange complex is appreciably smaller than the exchange calcium or the exchange magnesium. This is in general agreement with most of the investigations of solonized soils in North America. The content and the relative proportion of sodium in Alberta solonized soils are sometimes higher than in adjacent so-called "normal" soils. The solonized soils from the black soil zone used in this investigation contained more sodium than did the solonized soils of the drier brown soil zone.

Excessive leaching has not taken place in either the brown or the black soils. Only two of the nineteen brown soil profiles analyzed showed traces of exchange

hydrogen, but this feature was slightly more marked in the black soils. The solonized profiles indicate this to a greater extent than do the nonsolonized profiles.

The remaining horizons of eroded "slick spot" profiles in general contained larger amounts and proportions of sodium than did horizons of noneroded spots. Accumulations of soluble sulfates in the B₂ horizons of the eroded profiles are attributed to the extremely low permeability of the overlying B₁ horizons.

The so-called solonetz soils of Alberta do not belong to the true alkali soils but are alkalized to a lesser degree. The profile morphology is typically solonetzic but lacks the solonetz chemistry. These soils contain insufficient proportions of exchange sodium to be included in the sodium soils of Gedroiz. Some of the solonized soils of the black soil zone might be included in the sodium soils of de'Sigmond, but in general the solonetz soils of Alberta have the chemical composition of the "solonetz-like" soils of Glinka and of de'Sigmond.

REFERENCES

- (1) BARBER, H. H., AND KOLTHOFF, I. M. 1928 A specific reagent for the rapid determination of sodium. *Jour. Amer. Chem. Soc.* 50: 1625-1631.
- (2) BRAY, R. H. 1935 The origin of horizons in clay-pan soils. *Amer. Soil Survey Assoc. Bul.* 16: 70-75.
- (3) CARPENTER, E. J., AND STORIE, R. E. 1928 Soil survey of the Paso Robles Area, California. U. S. Bur. Chem. and Soils, Ser. 1928, No. 34.
- (4) ELLIS, J. H., AND CALDWELL, O. G. 1935 Magnesium clay "solonetz." *Trans. Third Internatl. Cong. Soil Sci.* 1: 348-350.
- (5) FIEGER, E. A., AND STURGIS, M. B. 1933 Profile studies of the coastal prairie soils of Louisiana, exchange and solution properties. *Soil Sci.* 38: 267-277.
- (6) GAMMON, N., GOLDEN, L. B., AND THOMAS, R. P. Comparison of methods of estimating the exchangeable cations and exchange capacity of soils. [To appear in *Soil Sci. Soc. Amer. Proc.* 7.]
- (7) HOLOWAYCHUK, N. 1932 Replaceable bases, hydrogen and base holding capacity of Alberta soils. *Canad. Jour. Res.* 7: 67-74.
- (8) JENNY, H., AND SMITH, G. D. 1935 Colloid and chemical aspects of clay-pan formation in soil profiles. *Soil Sci.* 39: 377-89.
- (9) KELLEY, W. P., AND BROWN, S. M. 1924 Replaceable bases in soils. Calif. Agr. Exp. Sta. Tech. Paper 15.
- (10) KELLEY, W. P., AND BROWN, S. M. 1925 Base exchange in relation to alkali soils. *Soil Sci.* 20: 477-495.
- (11) KELLEY, W. P. 1934 The so-called solonetz soils of California and their relation to alkali soils. *Amer. Soil Survey Assoc. Bul.* 15: 45-52.
- (12) KELLOGG, C. E. 1934 Morphology and genesis of the solonetz soils of western North Dakota. *Soil Sci.* 38: 483-500.
- (13) MITCHELL, J., AND RIECKEN, F. F. 1937 The chemical nature of some typical soil profiles of Saskatchewan, Canada. *Sci. Agr.* 18: 109-119.
- (14) MURPHY, H. F., AND DANIEL, H. A. 1934 The chemical and physical properties of normal and solonetz soils and their relation to erosion. *Soil Sci.* 39: 453-461.
- (15) NIKIFOROFF, C. C., AND DROSDOFF, M. 1943 Genesis of a clay-pan soil: I. *Soil Sci.* 55: 459-482.
- (16) RIECKEN, F. F. 1941 Some considerations in the magnesium cycle of weathering in solonetz soils. Abs. Doctoral thesis, University of Illinois, Urbana.
- (17) ROST, C. O. 1936 Characteristics of some morphological solonetz soils of Minnesota. *Jour. Amer. Soc. Agron.* 28: 92-105.

- (18) ROST, C. O., AND CHANG, P. C. 1941 Exchangeable bases of solonchak of the Red River Valley. *Soil Sci. Soc. Amer. Proc.* 6: 354-359.
- (19) ROST, C. O., AND MAEHL, K. A. 1943 Some solodized soils of the Red River Valley. *Soil Sci.* 55: 301-312.
- (20) SIGMOND, A. A. J. DE 1938 The Principles of Soil Science. Thomas Murby and Co., London.
- (21) STORIE, R. E. 1933 Profile studies of the solonetz soils of California. *Amer. Soil Survey Assoc. Bul.* 14: 43-46.
- (22) SUSHKO, S. Y. 1933 The role of absorbed magnesium in the formation of solonetz properties in soils. *Chem. Abs.* 27: 5458.
- (23) WYATT, F. A., AND NEWTON, J. D. 1927 Alberta soil profiles. *First Internatl. Cong. Soil Sci.* 4. 358-366.

ABSORPTION BY PLANTS OF PHOSPHORUS FROM A CLAY-WATER SYSTEM: METHODS AND ENSUING OBSERVATIONS

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The phosphorus content of the soil solution extracted from many fertile soils is very low, yet normal crops are produced. Contact effects between plant roots and soil particles have frequently been postulated to explain how plants obtain an adequate phosphorus supply from such soils. Parker (8), for example, has shown that corn plants will grow normally in culture solutions containing 0.25 p.p.m. PO_4 , provided this concentration is continuously maintained. On the other hand, growth was found to be restricted if the concentration was maintained at 0.1 p.p.m. PO_4 . The soil solution of many productive soils frequently contains considerably less than 0.1 p.p.m. of PO_4 . It was presumed, therefore, that in some soils there must be a contact effect between the root system and the solid phase before plants can absorb the phosphorus necessary for normal growth.

The concentration of phosphorus in a solution sufficient to maintain normal growth is dependent upon many factors, such as rate of growth, rate of renewal of the solution, area of root absorbing surfaces, and characteristics of the root systems. That plants can absorb phosphorus from very dilute solutions has been frequently demonstrated; however, the rate may not be sufficiently rapid and, thus, normal growth is perhaps restricted. Any comparison between continuously renewed solution cultures and soil solutions must presuppose that the character and area of the root absorbing surfaces are the same in both cases.

Soil solution data are at best arithmetic averages of the conditions which exist in soils. That the concentration of phosphorus in the solution extracted from a given soil is very low does not preclude the possibility of the presence within the soil of zones having a solution of considerably greater concentration in respect to phosphorus. Also, it is conceivable that during the process of extracting a soil solution, phosphorus may be removed from the solution as it is pushed past surfaces having different properties from those with which it originally had established an equilibrium.

No direct experimental evidence is available which demonstrates that more phosphorus is absorbed by plants as a result of a contact between the root and the solid phase of a soil. By and large, the theories concerning contact feeding have been proposed because of the apparent inadequacy of the soil solution theory. These theories predominately propose that the root exerts an influence, usually an excretion, which causes the phosphorus of the solid phase in close proximity with the root to dissolve readily.

Jenny and co-workers (5, 6, 7) have reported an interesting series of experi-

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ments concerned with the contact effects between plant roots and soil colloids. They have demonstrated that an interchange of cations takes place when roots are in contact with soil colloidal systems. Unfortunately anions were not considered in these investigations.

In the foregoing discussion no attempt was made to acknowledge the contribution of many investigators. The reader is referred to the discussion and review by Thomas (10) concerned with how ions pass from the soil to the root.

PURPOSE AND SCOPE OF INVESTIGATION

The purpose of this investigation was to obtain direct experimental evidence which would show whether increased absorption of phosphorus occurs as a result of contact between plant roots and soil particles. Since it is generally recognized that phosphorus exists in soils in several different forms, it seemed advisable at the outset to limit the scope of the study, so far as possible, to a single class or category of soil phosphorus. Also, the question as to whether the rate of absorption was adequate for normal plant growth was ignored. In view of the apparent success of Jenny and co-workers using clay-water systems in studying contact effects between roots and soil particles a similar system was adopted, namely, the clay fraction separated from a soil of the Davidson series. The Davidson clay was predominantly composed of kaolinite, gibbsite, and iron oxides, most of the organic matter having been eliminated by repeated treatments with hydrogen peroxide.

Undoubtedly, radioactive phosphorus is ideally applicable to studies of the type proposed. The uncertainty of a supply at the time this investigation was undertaken, however, necessitated the elimination of this possibility. It appeared inadvisable to apply to the problem at hand an excised root technique such as that developed by Hoagland and Broyer (4), since it did not seem possible to measure satisfactorily the changes in the phosphorus content of roots during periods of less than a week. Consequently a new technique was developed making possible the growing of plants under reproducible standard conditions in a clay-water system for periods of several weeks.

PHOSPHORUS ASSOCIATED WITH THE CLAY-WATER SYSTEM

Before the absorption of phosphorus from clay-water systems is considered it may be well to review briefly the chemistry of the phosphorus associated with these systems. The phosphorus associated with clay materials such as kaolinite and the hydrous oxides is readily released by hydroxyl and fluoride ions (2, 3, 9). On the other hand when phosphorus is absorbed by these materials there is a measurable release of hydroxyl ions. These phenomena are sometimes referred to as anion exchange. In other words, when phosphorus is absorbed by a clay system, there is an exchange between certain of the hydroxyl ions of the clay crystals and the phosphate ions in solution. At equilibrium the amount of phosphorus remaining in solution is related to the anion-exchange capacity, the amount of phosphorus on the surface, and the hydroxyl-ion concentration of the solution.

This distribution of phosphorus between the clay and the intermicellar liquid is illustrated by the following experiment. Six 2.5-gm. samples of colloid were each suspended in 200 ml. of water and placed in containers, where they were continually agitated by a gentle stream of CO_2 -free air passing through a fritted glass disc. Varying amounts of a sodium phosphate solution, pH 4.5, were added to each of the suspensions in amounts representing approximately 5, 10, 15, 20, 25, and 30 per cent of the saturation capacity. Collodion bags were introduced into each of the systems, and at intervals small aliquots were removed from the bags for analysis, and corresponding amounts of water replaced. Twenty-eight days after the start of this experiment 1.0 ml. of 0.1 *N* sodium hydroxide was added to each of the suspensions.

TABLE 1

Distribution of phosphorus between clay surfaces and the liquid phase of a clay-water system as a function of time, pH, and amounts of phosphorus added

P APPLIED AS APPROX. PER- CENTAGE SATU- RATION	COMPOSITION OF INTERMICELLAR LIQUID								
	Start	5 days		22 days			35 days*		
	P	P	pH	P	pH	K^\dagger	P	pH	K^\dagger
	p.p.m.	p.p.m.		p.p.m.			p.p.m.		
5	0.78	0.014	5.6	0.002	5.1	0.85×10^{-3}	0.059	6.9	1.6×10^{-3}
10	1.55	0.022	5.5	0.006	5.2	0.74×10^{-3}	0.069	6.7	1.9×10^{-3}
15	2.33	0.037	5.4	0.011	5.3	0.80×10^{-3}	0.079	6.6	2.1×10^{-3}
20	3.10	0.084	5.7	0.026	5.7	1.2×10^{-3}	0.345	6.6	0.61×10^{-3}
25	3.88	0.144	5.6	0.030	5.6	1.1×10^{-3}	0.262	6.8	1.8×10^{-3}
30	4.65	0.448	6.0	0.077	5.9	1.0×10^{-3}	0.533	6.5	0.51×10^{-3}

* Sodium hydroxide was added on the 28th day.

$$\dagger K = \frac{C_{\text{OH}}(\text{solution}) \times C_{\text{H}_2\text{PO}_4}(\text{surface})}{C_{\text{OH}}(\text{surface}) \times C_{\text{H}_2\text{PO}_4}(\text{solution})}$$

In table 1 are given the phosphorus concentration and pH values of the intermicellar liquids at the start and 5, 22, and 35 days later. These data show that a final equilibrium between the phosphorus in solution and that associated with the colloid is attained only after a long time. Black (1) assumed that this delay resulted from a slow penetration of the phosphorus into the interior of the clay crystals. Possibly one factor which is generally overlooked in this regard is the slowly changing hydroxyl concentration as a result of exchange with the phosphate ions and also of changes in the exchange hydrogen. The equilibrium (mass action) constants calculated for the 22- and 35-day data were approximately 10^{-3} . The agreement between these values for the various sets of data was relatively close, but unfortunately the estimation of the OH-ion concentration by pH measurements of unbuffered solutions permits errors of a rather large magnitude.

As previously stated, 0.1 p.p.m. PO_4 (0.03 p.p.m. P) is about the minimum concentration at which corn plants grow normally in a nutrient solution, where

the phosphorus concentration is held approximately constant by continuous renewal. Consequently it was deemed advisable to hold the concentration of phosphorus in the intermicellar liquid of the clay-water systems well below 0.03 p.p.m. P when studying the contact effects of roots and soil particles. The data in table 1 indicate that such low concentrations exist only under acid conditions or at a low degree of saturation of the colloid in respect to phosphorus. It also appeared advisable to work with systems in which equilibrium was well established before the plants were introduced.

METHOD OF GROWING STANDARD PLANTS

The growing of uniform plants for studies such as have been proposed in this paper merits considerable attention. With the common greenhouse methods, the effect of the various seasons makes it difficult to have a continuous supply of plants with similar physiological characteristics. For this reason, all of the cultural operations were carried out in a constant-temperature chamber artificially illuminated with fluorescent lights.

The light chamber was a converted constant-temperature room. A panel carrying fluorescent lights was suspended over a table on which the plants were grown. Alternate white and daylight, 30-watt, fluorescent light tubes were closely spaced on the panel. The distance of the panel from the growing plants was so adjusted that light intensity available to the leaf surfaces was 800 to 900 foot-candles. The lights were controlled by an automatic time switch providing for 16 hours of light and 8 hours of darkness. The temperature within the chamber was maintained at 25° C. The humidity was not controlled, but frequent sling psychrometer readings showed the relative humidity usually to be about 50. No provision was made for introducing new air into the chamber except as the door was opened to allow people to pass in or out. It is not inconceivable that at times CO₂ was a limiting factor to plant growth in the chamber.

Barley (Wis. H 35-7-2-1-3) was chosen as the experimental plant in all contact feeding experiments, though preliminary trials with crimson clover, tomatoes, and buckwheat indicated that they also could be satisfactorily handled in the light chamber. The barley plants were supported on corks. Each of the corks containing four plants was considered as an experimental unit. The phosphorus content of the nutrient solution was controlled so that the plants in each cork when 5 weeks old contained approximately 3 mgm. of phosphorus. Two-gallon (7-liter) earthenware crocks were used to contain the nutrient solution, and three corks of plants were grown in each crock. In order to obtain a greater degree of uniformity in the composition of the plants, the corks were systematically interchanged daily. When about 3 weeks old, some of the barley plants tended to lodge. Considerably more uniform growth was obtained when the plants were supported.

Indications were that the osmotic pressure and the nitrogen content of the usual nutrient solution were too high for satisfactory growth with the limiting light conditions available to the plants. Satisfactory growth was obtained when

the germinated seedlings were started in a nutrient solution of the following composition:

$0.5 \times 10^{-3} M$	magnesium sulfate
$0.5 \times 10^{-3} M$	calcium nitrate
$1.0 \times 10^{-3} M$	calcium sulfate
$0.7 \times 10^{-3} M$	potassium sulfate

Generally 1.5 mgm. of phosphorus as NaH_2PO_4 per liter of nutrient solution was also added to this solution. After the plants had been growing for 2 weeks, additional MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, and K_2SO_4 were added in amounts sufficient to double the original concentration of these salts in the solution. When the plants were a week old, 5 cc. of a solution containing 100 mgm. per liter of MnCl_2 and 50 mgm. per liter of H_3BO_3 was added to each 7 liters of nutrient solution. At weekly intervals, 2 cc. of a 0.25 per cent solution of ferric tartrate was added to each 7 liters of solution.

Each cork of four barley seedlings had approximately the following dry weight and phosphorus content when harvested at 5 weeks of age:

Dry weight of tops	0.4 to 0.5 gm.
Dry weight of roots	0.1 to 0.13 gm.
Phosphorus content of tops	1.9 to 2.2 mgm.
Phosphorus content of roots	0.5 to 0.6 mgm.

METHOD OF GROWING PLANTS IN CLAY-WATER SYSTEMS

Two techniques were developed for growing plants in clay-water systems and for studying the absorption of phosphorus. In one, the corks containing 5-week-old seedlings, grown as described in the preceding section, were transferred to a vessel where the roots were directly in contact with a clay-water system. In the other, the seedling roots were enclosed in collodion bags which, in turn, were inserted in a clay-water system.

Preliminary experiments demonstrated that it was necessary to give consideration to the cations associated with the clay; otherwise, deficiency symptoms, especially those of potassium, were apparent within a very few days after the plants were transferred to the clay-water system. Satisfactory growth and cation nutrition of plants were obtained when the clay-water systems were prepared by the following procedure.

Two-hundred-gram lots of soil from which the clay was to be extracted were treated at boiling temperatures with hydrogen peroxide until no further reaction with the organic matter was apparent. Ammonium hydroxide was added, the soil suspension dispersed with a rotary stirrer and diluted to a volume of 3 gallons with water. After standing for 8 hours the top 5 cm. of suspension was syphoned off. The water removed was replaced, the suspension shaken, allowed to stand 8 hours, and again the top 5 cm. syphoned off. This process was repeated until the greater part of the clay in the original suspension had been removed.

The extracted clay was coagulated by adding potassium chloride followed by

bubbling CO_2 into the suspension. Then the clay was subjected to prolonged electro dialysis, after which it was dispersed with a mechanical stirrer to break up the lumps formed. The pH of this clay suspension was adjusted to about 5.2 by adding the required amount of potassium hydroxide over a period of about a week.

Sufficient colloid was then removed to make 100 ml. of a 1 per cent clay suspension, and after a week was allowed for equilibrium to become established the phosphorus concentration of the intermicellar liquid was determined. When the

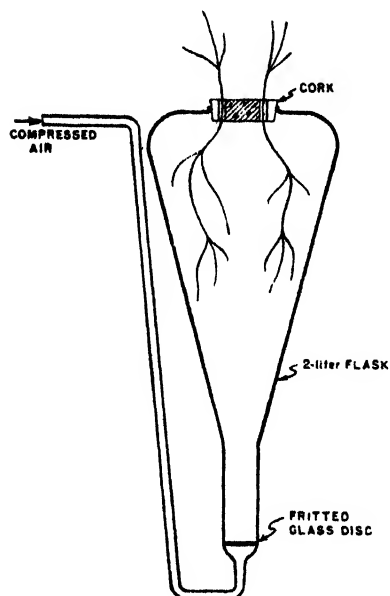


FIG. 1

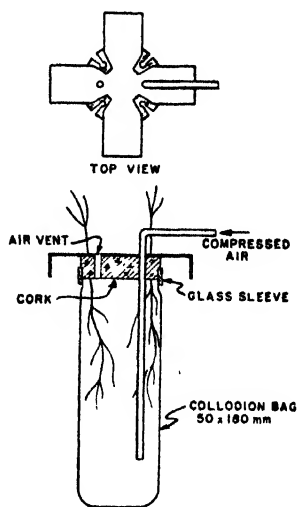


FIG. 2

FIG. 1. CULTURE VESSEL DESIGNED FOR THE GROWING OF PLANTS IN CLAY-WATER SYSTEMS

FIG. 2. ARRANGEMENT USED FOR GROWING PLANTS IN CLAY-WATER SYSTEMS BUT WITH THEIR ROOTS IN A COLLODION BAG

concentration was not approximately 0.005 p.p.m., adjustments were made in the pH or the phosphorus content of all the clay. This clay was then ready for use.

Clay-water suspensions containing from 0.75 to 1.0 per cent of clay particles were found to be satisfactory for growing plants. A convenient method of making dilutions of known concentration from the bulk sample of clay prepared as described above is by means of specific gravity measurements. The bulk sample was made to a definite volume, and its weight and temperature were determined. The total weight of colloid was calculated from the formula:

$$\text{Weight of clay} = \frac{2.32 (\text{weight clay suspension} - \text{volume} \times \text{density of } \text{H}_2\text{O})}{2.32 - \text{density of } \text{H}_2\text{O}}$$

Uniform aliquots containing the desired weight of clay were then drawn while the suspension was being stirred with a rotary stirrer. Before these aliquots

were finally diluted 5 ml. each of 0.025 M K_2SO_4 , 0.025 M $Ca(NO_3)_2$, and 0.0125 M $MgSO_4$ were added for each liter of the final volume of clay-water system.

Special vessels were designed to eliminate possible difficulties that might occur from the settling out of the clay-water systems and to assure a uniform contact between the clay particles and the plant roots. These vessels were made from 2-liter flasks and are illustrated in figure 1. The stream of air which is forced through the fritted glass disc at the bottom of the vessel keeps the clay particles in continuous motion and also aerates the solution. One cork containing the plants was inserted in each of these vessels.

Figure 2 illustrates the arrangement used when a collodion bag containing the plant roots was introduced into the clay suspension. This arrangement was always used in conjunction with the vessel illustrated in figure 1. When preparing this arrangement it was necessary to remove the plant from the corks on which they were originally supported and fix them to the specially designed cork. The collodion bag (50 by 180 mm.) was then fitted into place around the roots and sealed to the cork with a glass ring. The solution inside the collodion bag was aerated by means of the glass tube extending into it. Damage to the bags was very infrequent even when plants were grown in them for 3 weeks.

EFFECT OF CONTACT BETWEEN CLAY PARTICLES AND PLANT ROOTS ON ABSORPTION OF PHOSPHORUS

Preliminary experiments showed that when 5-week-old barley plants were transferred to a clay-water system having a phosphorus content of 0.005 p.p.m. in the liquid phase and allowed to grow there for 2 weeks the phosphorus content of the plants increased significantly. Experiments of this type, however, do not necessarily demonstrate that contact exchange between the roots and soil particles takes place. Consequently, an experiment was conducted in which it was possible to compare the amounts of phosphorus absorbed by plants grown with roots directly in contact with a clay-water system and by plants grown with roots in collodion bags suspended in clay-water systems. The assumption, *a priori*, was made that any differences would be the result of contact effects between the roots and clay particles.

Space and equipment available limited the number of observations in a single experiment to 12. The experimental design chosen was a 2 by 2 factorial with three replications. The treatments were the two techniques of growing the plants, (a) roots in the clay-water system, (b) roots in collodion bags, and clay-water systems at two pH levels (a) 5.75, and (b) 6.15. The clay-water systems at pH 6.15 were obtained by adding $Ca(OH)_2$ to systems having a pH of 5.75. Nineteen corks of four barley plants each were grown to an age of 5 weeks, and 12 of these corks were selected at random and used in the experiment. The remaining seven corks were harvested and considered as checks. The duration of the experiment was 3 weeks from the time the treatments were started. When the plants were harvested the roots were kept separate from the tops, but the different plants in a single cork were not segregated. The plant material was dried at 70° C., weighed, and the phosphorus content of the samples determined.

For a record of the phosphorus concentration of the intermicellar liquids in the various cultures, samples were drawn every third day in the following manner: In those cultures where the roots were growing enclosed in collodion bags the solution within the bags was sampled; in the other cultures, small collodion bags were introduced into the system. The intermicellar liquids were found to

TABLE 2
Effect of contact feeding and pH of clay-water system on phosphorus content of barley seedlings

PHOSPHORUS CONTENT OF SEEDLINGS

CLAY-WATER SYSTEM, pH 5.75		CLAY-WATER SYSTEM, pH 6.15		CHECK PLANTS
Roots in collodion bag—no contact feeding	Roots in clay—contact feeding possible	Roots in collodion bag—no contact feeding	Roots in clay—contact feeding possible	
mgm.	mgm.	mgm.	mgm.	mgm.
<i>Tops of plants</i>				
2.59	2.15	2.43	2.45	2.17
2.39	2.89	2.37	2.53	2.03
2.36	2.32	2.70	2.20	2.35
				1.87
				1.82
				2.11
				2.17
Av.: 2.45	2.45	2.50	2.39	2.07
<i>Roots of plants</i>				
0.423	0.395	0.477	0.463	0.561
0.465	0.481	0.463	0.502	0.515
0.382	0.453	0.571*	0.494	0.599
				0.473
				0.547
				0.584
				0.509
Av.: 0.423	0.443	0.504	0.486	0.541
<i>Sum of tops and roots</i>				
2.873	2.893	3.004	2.876	2.611

contain 0.005 to 0.008 p.p.m. P. No consistent difference in phosphorus concentration was found between the solutions taken from bags with and without plant roots.

The detailed results obtained from the experiment are given in table 2. These data are presented in this form to indicate the variability of the experimental material and the magnitude of the changes which occurred as a result of growing plants in clay-water systems.

The data of table 2 were subjected to a detailed statistical analysis. The

various comparisons and the differences which were found significant at 19:1 odds are indicated in table 3. There were two sets of comparisons which could be made; namely, the differences between the factors considered in the factorial experiment and the comparisons between the check plants and those of the four treatments of the factorial experiment. Three separate statistical analyses were made: the tops of the plants considered alone, the roots considered alone, and the sum of the tops and roots.

There was only one significant difference found in the comparisons allowed by the factorial experiment. The roots of the plants growing in the clay-water system at pH 5.75 contained significantly less phosphorus than those growing in the clay-water system at pH 6.15. There was no indication of a significant difference between the amount of phosphorus in the plants growing with roots directly in the clay-water system and those growing with roots in collodion bags;

TABLE 3
Differences between comparisons of data in table 2 and their significance

COMPARISONS	TOPS		ROOTS		WHOLE PLANT	
	Differences	Significance	Differences	Significance	Differences	Significance
No contact feeding vs. contact feeding	+0.11		+0.006		+0.108	
pH 5.75 vs. pH 6.15	-0.01		-0.230	*	-0.114	
Interaction of pH \times feeding	+0.11		+0.148		+0.148	
No contact feeding vs. check	+0.81	*	-0.155	*	+0.655	*
Contact feeding vs. check	+0.70	*	-0.135	*	+0.547	
pH 5.75 vs. check	+0.76	*	-0.216	*	+0.544	
pH 6.15 vs. check	+0.75	*	-0.092		+0.658	*

* Indicates a significant difference, at 19:1 odds.

therefore, there were no contact effects between roots and soil particles which influenced the absorption of phosphorus.

The comparisons between the checks and the various treatments show the overall changes in phosphorus resulting from growing the plants for 3 weeks in clay-water systems. The tops of the plants from all treatments contained significantly more phosphorus than the checks. The roots of the treated plants contained less phosphorus than the checks. The difference between the checks and the plants growing in the clay-water systems at pH 6.15 was small and not significant. When the plants as a whole are considered (sum of roots plus tops) the treated plants contained more phosphorus than the checks. The comparisons of no contact feeding vs. check and pH 6.15 vs. check were significant. The other two comparisons were not significant, though they closely approach significance.

The loss of phosphorus from the root systems was of some interest. In addition to a loss by translocation from roots to tops, possibly there was damage to the root systems which caused a sloughing off of root tissues. On the other hand, it is also possible that the high phosphorus-adsorbing power of the clay-

water systems, especially at the lower pH, regulates to some degree the amount of inorganic phosphorus that may exist in the root system. Some support of the latter contention may be found from a comparison of the percentages of phosphorus in roots of the plants growing in clay-water systems at different pH values. The percentages of phosphorus were 0.233 for the pH 5.75 system and 0.258 for the pH 6.15 system. The difference between these percentages was found to be significant.

The results of another experiment similar to the foregoing are given in table 4. These data again show a decrease in the phosphorus content of the roots

TABLE 4

Loss of phosphorus from barley seedlings having a high percentage of phosphorus, when placed in clay-water systems

	PHOSPHORUS CONTENT OF SEEDLINGS				
	Tops		Roots		Whole plant
	<i>per cent</i>	<i>mgm.</i>	<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>
Check plants	0.67	2.42	0.84	0.81	3.23
	0.65	2.37	0.76	0.81	3.18
	0.64	2.00	0.79	0.77	2.77
	0.64	2.29	0.75	0.79	3.28
Average	0.65	2.27	0.785	0.795	3.06
Roots in clay system	0.42	2.00	0.40	0.53	2.53
	0.40	1.81	0.41	0.49	2.30
	0.42	2.45	0.42	0.63	3.08
Average	0.41	2.09	0.41	0.55	2.64
Roots in collodion bag	0.45	2.34	0.46	0.55	2.89
	0.43	2.32	0.44	0.61	2.93
	0.44	2.14	0.41	0.50	2.64
Average	0.44	2.27	0.44	0.55	2.82

when seedlings are placed in clay-water systems. In this experiment there was no transfer of phosphorus from the clay-water system to the plants; instead, there was a loss from the plants to the clay-water system. When the plants of this experiment were introduced into the clay-water systems they were younger than those used in the previous experiment and thus the percentage of phosphorus in check plants was almost twice as great. The duration of this experiment was only 2 weeks.

The decrease in the phosphorus content of the roots of plants growing in clay-water systems as shown by these experiments gives some support to the following hypothesis: The phosphorus associated with the roots and that associated with the clay each tends independently to establish an equilibrium with the phos-

phorus in solution in the intermicellar liquid of the clay-water system. If the phosphorus equilibrium potential of the roots is higher than that of the clay, phosphorus will migrate from root to clay; if the potential of the clay is higher, the movement will be in the opposite direction.

DISCUSSION

This study concerned with the absorption of phosphorus from clay-water systems, although for the most part preliminary, has brought out several interesting points. A question might be raised about the relationship between soil conditions and those of the cultures. In these cultures most of the clay particles were in a state of continual agitation, and therefore the periods of contact between particles and roots were presumably short. Certainly the appearance of the roots of plants growing in clay-water systems suggested that this environment was not wholly ideal.

The soil is composed of discrete particles and aggregates of variable composition. Some of these may have a relatively high phosphate solution potential whereas others may be just the opposite. A root absorbing surface immediately adjacent to a particle having a high phosphate solution potential will show a high rate of phosphorus absorption, whereas a root next to, let us say, a gibbsite particle may impart phosphorus to the particle. There is no reason to suppose that all parts of a root system are doing the same thing; quite the opposite seems probable. If a sufficient ratio of the root absorbing surfaces is adjacent to particles having a high phosphate solution potential the plant as a whole will be expected to get along all right.

Perhaps something could be learned if a method of microscopic examination of soils were available which would reveal the phosphate concentrations that are set up in the immediate aqueous environment of soil particles.

SUMMARY

Standard experimental plants, grown under artificial lighting, were studied to determine their absorption of phosphorus from clay-water systems. Preliminary results with barley seedlings gave no evidence of a contact exchange or other contact effect between plant roots and clay particles which affects the rate of absorption of phosphorus from clay-water systems. Apparently, under certain conditions, roots of plants lose phosphorus to a surrounding clay-water system.

REFERENCES

- (1) BLACK, C. A. 1942 The penetration of phosphate into the kaolinite crystal. *Soil Sci. Soc. Amer. Proc.* (1941) 6: 157-161.
- (2) DEMOLON, A., AND BASTISSE, E. 1934 Contribution a l'etude de la mecanique chimique des anions dans le sol. *Ann. Agron.* 4: 53-76.
- (3) DICKMAN, S. R., AND BRAY, R. H. 1941 Replacement of adsorbed phosphate from kaolinite by flouride. *Soil Sci.* 52: 263-273.
- (4) HOAGLAND, D. R., AND BROYER, T. C. 1936 General nature of the process of salt accumulation by roots with description of experimental methods. *Plant Physiol.* 11: 471-507.

- (5) JENNY, H., AND OVERSTREET, R. 1939 Cation interchange between plant roots and soil colloids. *Soil Sci.* 47: 257-272.
- (6) JENNY, H., OVERSTREET, R., AND AYRES, A. D. 1939 Contact depletion of barley roots as revealed by radioactive indicators. *Soil Sci.* 48: 9-24.
- (7) JENNY, H., AND OVERSTREET, R. 1939 Surface migration of ions and contact exchange. *Jour. Phys. Chem.* 43: 1185-1196.
- (8) PARKER, F. W. 1927 Recent studies on the phosphate content of the soil solution and its relation to the phosphorus nutrition of the plant. *Proc. 1st Internatl. Cong. Soil Sci.* 2: 384-395.
- (9) STOUT, P. R. 1940 Alterations in the crystal structure of clay minerals as a result of phosphate fixation. *Soil Sci. Soc. Amer. Proc.* (1939) 4: 177-182.
- (10) THOMAS, W. 1930 The feeding power of plants. *Plant Phys.* 5: 443-489.

AN ACCURATE METHOD FOR DETERMINING VOLUME OF SOIL CLOUDS¹

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Volume weight of soil is used to compute the weight of the furrow-slice of certain soils, the weight of an acre-foot of soil, and the weight of a genetic soil horizon. Also it is a means of determining total porosity of a soil. It indicates whether, with regard to physical condition, the soil meets requirements as a seedbed for plants.

By using the soil-core method for determining volume weight (5, pp. 115-116; 10) it is possible to differentiate between different-sized pores, but this method has the advantage of possible compression of the soil when the sample is taken. Gross volume of a soil sample has been ascertained by boring a hole in the soil and filling it with a known amount of sand or water (3, 4). Perry (6) coated soil aggregates with paraffin and suspended them in a series of $ZnCl_2$ solutions of different densities until an equilibrium was reached between soil and solution. The most common method of determining volume weight is to weigh an oven-dry soil clod in air and in water after it has been coated with a thin layer of paraffin (1, 8, 9). Some workers have used mercury instead of water displacement for volume determination (2, 7).

The purpose of this paper is to report a refinement of the paraffin immersion technique for determining the volume of soil clouds.

APPARATUS

The apparatus for measuring the volume of soil clouds is shown in figure 1. It consists of a 50-ml. burette connected to a wide-mouthed (38-mm.) filter funnel by a piece of pressure tubing and mounted on a burette stand. A specially constructed cork stopper fits in the mouth of the filter funnel. This stopper has a small wire basket suspended from the bottom, and has a graduated glass tube passing through it. It is encircled by a ledge of De Khotinsky cement, which permits equal volume displacement each time the stopper is placed in the funnel.

Particular attention should be given the construction and assemblage of the cork stopper. The hole in the stopper for the glass tube should be small enough to allow close contact, in order to prevent leakage, and should flare out at the bottom in order that air bubbles may not be trapped beneath the stopper. The bottom of the glass tube should flare out so it will fit the slope of the hole in the bottom of the stopper. The glass tube with line etched on the outside is placed

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in the stopper and the stopper fitted snugly in the filter funnel. By rotating the funnel and stopper and letting melted De Khotinsky cement drop on the stopper just above the glass, a ledge of cement is formed.

The pressure tubing should be attached firmly to the ends of the burette and funnel with small pieces of wire, to avoid slippage and change of volume in the

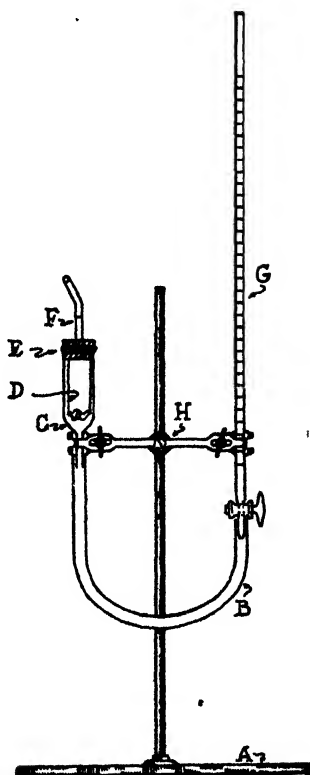


FIG. 1. SOIL VOLUMETER FOR DETERMINING VOLUME OF SOIL CLODS

- | | |
|-------------------------------------|--|
| A. Burette support base. | E. Ledge of De Khotinsky cement on |
| B. Pressure tubing. | cork for consistent and uniform place- |
| C. Filter funnel (38 mm. diameter). | ment of cork stopper. |
| D. Wire basket attached to cork for | F. Glass tubing with calibration line |
| supporting soil clods. | etched on outside. |
| | G. Fifty-milliliter burette. |
| | H. Double burette holder. |

system. Fluctuation in volume of the system must not be permitted; otherwise, the volume readings will be inaccurate.

In filling the system with water, care must be taken to eliminate all air bubbles. This is done by leaving the stopcock to the burette open, and then forcing the water in and out of the system by blowing on the open end of the glass tube. The operating level of the water should be at the volume line on the glass tube, and 6 to 8 ml. above this in the burette.

PROCEDURE AND RESULTS

Oven-dry soil clouds about 1 inch in diameter are coated with a thin layer of paraffin by dipping in melted paraffin at a temperature of 60° C. The soil clouds are weighed both before and after the coating is applied.

In order to determine the volume of soil clouds the volumeter is placed on a work bench of such height that the open end of the glass tube is level with the operator's mouth. The water level is adjusted to the volume line on the glass tube by opening and closing the stopcock to the burette. A reading on the burette is obtained and recorded. The stopcock is opened, and pressure is applied to the system through the open end of the glass tube. The stopcock is closed after the volume of water forced into the burette is greater than the volume of the soil cloud to be introduced into the funnel. The stopper is then removed from the funnel and a soil cloud placed in the wire basket. The stopper with soil cloud suspended is placed in the funnel, the water level is readjusted to the volume line

TABLE 1
Volume of a soil cloud as determined by two methods

DETERMINATION NUMBER	VOLUME OF CLOUD	
	Burette method	Cylinder method
	cc.	cc.
1	12.51	13.0
2	12.51	12.0
3	12.55	13.0
4	12.52	13.0
5	12.52	11.5

on the glass tube by opening and closing the stopcock, and a second burette reading is taken and recorded. The difference between the first and second readings represents the volume of the soil cloud and paraffin coating.

The volume weight of the soil is then calculated by means of the following equation:

$$\text{Volume weight} = \frac{W}{V - (1.11 \times Pw)}$$

where W = weight of oven-dry soil

V = volume of soil cloud and paraffin coating

Pw = weight of paraffin coating

The factor 1.11 represents the volume of 1 gm. of paraffin. The density of paraffin used in deriving this factor was 0.9.

A number of volume determinations were made on the same cloud both by the proposed method and by the graduated-cylinder method. The data, listed in table 1, show that a very accurate volume determination can be obtained with the soil volumeter.

REFERENCES

- (1) BROWN, B. E., MACINTIRE, W. H., AND CREE, W. F. 1910 Comparative physical and chemical studies of five plots, treated differently for twenty-eight years. *Pa. Agr. Exp. Sta. Ann. Rpt.* 1909-10: 96-97.

- (2) FROSTERUS, P., AND FRAUENFELDER, H. 1926 Apparatus for soil volume determination. 1925. *Internatl. Rev. Sci. and Pract. Agr. [Rome]* 3: 100-104.
- (3) HARLAND, M. B., AND SMITH, R. S. 1928 Volume weight of certain field soils. *Jour. Amer. Soc. Agron.* 20: 533-541.
- (4) ISRAELSON, O. W. 1918 A new method of determining volume weight. *Jour. Agr. Res.* 13: 28-35.
- (5) KING, F. H. 1901 *Physics of Agriculture*. Madison, Wis.
- (6) PERRY, E. P. 1943 A simple rapid method of determining the apparent density of soil aggregates. *Soil Sci. Soc. Amer. Proc.* (1942) 7: 409-411.
- (7) PURI, A. N., TAYLOR, E. M., AND ASGHAR, A. G. 1934 A new apparatus for measuring soil shrinkage. *Soil Sci.* 37: 59-63.
- (8) SHAW, C. F. 1917 A method for determining the volume weight of soils in field condition. *Jour. Amer. Soc. Agron.* 9: 38-42.
- (9) TRNKA, R. 1914 Eine Studie über einige physikalischen Eigenschaften des Bodens. *Internatl. Mitt. Bodenk.* 4: 363-387. (Abs. *Exp. Sta. Rec.* 33: 420.)
- (10) VEIHMEYER, F. J. 1929 An improved soil sampling tube. *Soil Sci.* 27: 147-152.

THE IMPORTANCE OF OXYGEN IN THE NUTRIENT SUBSTRATE FOR PLANTS—RELATION OF THE NITRATE ION TO RESPIRATION¹

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The fact that the assimilation of nitrates by plants is associated with an adequate supply of available carbohydrates has been regarded (8) as indicating that an intimate relationship exists between the processes of sugar respiration and nitrate reduction. There is considerable experimental evidence in substantiation of such a relationship. It then follows that simultaneously with the assimilation of nitrates there should be a stimulation of respiratory carbon dioxide production commensurate with the rates of nitrate assimilation. Such a stimulation of carbon dioxide production has been shown for the alga *Chlorella* by Warburg and Negelein (14). Hamner (5) also found an increased carbon dioxide production with accelerated rates of nitrate reduction by actively growing young wheat and tomato plants.

Hoagland and Broyer (6) and Steward and Preston (13) have stressed the importance of the general metabolic activities of the root in ion absorption and accumulation and its dependence upon an adequate oxygen supply. It has been shown (4) that the oxygen requirement of plants varies greatly from species to species when grown in culture solutions of the same composition, and in a previous report (12) it was suggested that in soybean roots the aerobic oxygen supply could be supplemented by the oxygen derived from the reduction of absorbed nitrate ions in the roots. The chief purpose of the present report is to give further evidence in support of this suggestion. Since it has been shown that the level of available oxygen in a nutrient substrate is a determinative factor in the rate of nitrate-ion absorption and assimilation, a method is available for the investigation of this question.

METHODS

For a study of respiratory rates of the roots, the methods previously described (4) were employed with a modification of the apparatus to permit the measurement of the CO₂ produced. The plants were grown in 2.6 liters of solution in a wide-mouthed bottle closely fitted with a large rubber stopper. The axis of the plant was supported inside a glass tube, which was inserted through the stopper and dipped below the surface of the solution in the bottle. A water seal was thus formed around the root crown. Inlet and outlet tubes for solution and gas mixture were also provided to form a system isolated from the atmosphere for the maintenance of a constant oxygen tension and renewal of solution by con-

¹ Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of plant physiology.

tinuous flow. The CO_2 produced by the roots was removed from the culture solution by the aerating gas mixture. It was absorbed by a strongly alkaline solution wetting the surface of glass wool in a flask connected to the gas-exit tube of the special culture vessel.

The gas-absorbing vessel was a 125-ml. Erlenmeyer flask containing a wad of fine glass wool of about 2-ml. volume. The flask, with the wool inside, had previously been calibrated with distilled water. The flask was fitted with a two-hole rubber stopper carrying an inlet tube and a soda-lime tube for gas exit. Twenty milliliters of CO_2 -free 2 *N* NaOH was run into a dry, calibrated flask and the vessel introduced into the gas train after the culture solution. The 1-cm. head of alkali exerted a negligible back pressure upon the level of solution in the culture vessel. Efficiency of CO_2 absorption was insured by thoroughly wetting the glass wool with strong alkali to provide a large surface for contact of the effluent gas with the absorbent. Such a system was used in place of the conventional absorption tower because of the necessity of maintaining essentially atmospheric pressure in the culture vessel to keep the solution at the original level. This enabled the use of the continuous solution flow with the water-seal system for isolation of the roots (4), without the interference of the back pressure resulting from the use of an absorption tower.

Carbon dioxide must be determined by a direct analysis, since the concentration of the alkali required for efficient absorption of the CO_2 is too strong for an accurate back-titration for the relatively low carbonate-ion concentration. The presence of a large glass surface may also lead to a reaction between the glass wool and the alkali and thus introduce an appreciable error in the titrimetric determination of small amounts of CO_2 .

The direct analysis of the CO_2 was made on a suitable aliquot of the strong alkali after dilution to the previously calibrated volume. The manometric Van Slyke apparatus was used according to the method of Peters and Van Slyke (10, p. 270). The values for the temperature coefficients given by these workers for urinary CO_2 were checked against standard sodium carbonate to within 0.05 mole CO_2 per liter absolute error. It was imperative to use an alkali free from carbonates, but this was easily obtained by filtering 50 per cent NaOH and diluting with freshly boiled water. The diluted alkali was stored in a CO_2 -free atmosphere and measured directly into the absorption flask when needed. Blanks were run with each set of determinations. The blanks were exact duplicates of the cultures except that instead of the plants, solid glass rods were inserted inside the glass tube supports in the rubber stopper of the special culture vessel. A measured volume (3) of the same gas mixture used for aeration of the cultures was passed through the nutrient solution in the blanks and absorbed by the strong alkali in a similar absorption flask. Thus a correction could be made for any CO_2 in the alkali or any present in the gas train that might have leaked through the rubber connections of the gas stream.

The CO_2 that remained in the nutrient solution at the end of the period of aeration was determined by analysis of an aliquot of the nutrient solution according to the Van Slyke method for dissolved gases (10). The total root respira-

tion was taken as the sum of the CO_2 absorbed in the alkali and that left in the solution, including any bicarbonate present.

Absorption rates were measured by the usual technique of analysis of the solution before and after contact with the root system for the desired interval. Nitrates were determined colorimetrically by a phenoldisulfonic acid reagent. Sodium peroxide was found useful in destroying the interfering leaf pigments before reaction with phenoldisulfonic acid. Ammonium and total nitrogen were determined colorimetrically by Nessler's reagent. Digestion for total nitrogen was made with Ranker's reagents. Stabilization of the colored colloid was obtained up to 4 p.p.m. of ammonium N and when a 10 per cent Rochelle salt solution was added in the proportion of 1 ml. per 100 ml. of Nesslerized solution.

EXPERIMENTAL

Eighteen separate series of experiments were carried out with soybeans, oats, and tomato plants. To obtain a clearer evaluation of the influence of nitrate-N metabolism upon root respiration, the plan of experimentation previously reported (4) was broadened to include three different nitrogen-nutrition treatments at each of the different oxygen levels. Cultures of soybean plants were grown in a *complete solution* [formula I of Shive and Robbins (11)] containing nitrogen only as nitrate at the respective oxygen levels of 0, 4, 8, and 16 p.p.m. of dissolved oxygen. After 23 days of such treatment, two sets of cultures at each of the oxygen levels were transferred to a solution without nitrogenous salts [the $\text{Ca}(\text{NO}_3)_2$ being replaced with CaCl_2], the oxygen treatment being continued as before. The third set of cultures was continued as before with nitrate-N treatment at each oxygen level. After 10 days of this treatment the cultures supplied with nitrate-N were transferred to fresh complete solution for two consecutive 48-hour intervals, the solutions and the CO_2 -absorption flasks being changed at the end of the first and second 48-hour intervals to permit measurement of the rate of nitrate absorption and of CO_2 production. One set of the cultures without nitrogen, at each oxygen level, was transferred to fresh solution and CO_2 production determined. The other set was transferred to fresh complete solution for the determination of the rates of respiration and of nitrate absorption during the following two 48-hour intervals. The three sets of cultures are hereafter designated as follows: those kept on complete solution are referred to as the "plus-N cultures," those depleted of nitrate-N for 10 days prior to the test intervals are designated as the "minus-N cultures," and those returned to the complete solution for the two 48-hour test intervals after being depleted of nitrates are called the "minus-N to plus-N cultures."

Consideration may first be given to the highly significant effect of different oxygen treatments on the CO_2 production of the roots given an adequate supply of nitrates (plus-N plants). Total CO_2 production was highest at zero oxygen tension and lowest at 4 p.p.m. The respiration rate then rose slightly to a secondary maximum at 16 p.p.m.

The minus-N plants show a different type of relationship between CO_2 output

and oxygen tension from that obtained with the plus-N plants. The respiration of the roots is then directly related to the oxygen tension of the substrate that is characteristic of the aerobic phase of respiration, the CO_2 production being lowest at the lowest oxygen tension (0 p.p.m.) and highest at the highest oxygen tension (16 p.p.m.). The respiration rate, moreover, of the minus-N roots at each oxygen level is always less than the value for the corresponding plus-N culture.

The minus-N to plus-N plants have values for respiratory CO_2 intermediate between those for the plus-N and the minus-N cultures measured during the same interval. It is evident that the higher rate of respiration of the plus-N plants at each oxygen level is associated with the presence of a supply of nitrate ions. This is emphasized by the fact that in experiments in which ammonium nitrogen was substituted for the nitrate nitrogen in the plus-N cultures, the yield of respiratory CO_2 was always lower than it was from the corresponding cultures supplied with nitrate as the source of nitrogen, the CO_2 produced by the ammonium nitrogen cultures approaching in value that from corresponding minus-N cultures. It is significant that the lower rates of respiratory CO_2 produced when nitrate nitrogen is replaced by ammonium nitrogen in the nutrient substrate are regarded by Arnon (1) not merely as the substitution of one source of nitrogen for another but as the possible result of depriving the plant of an oxidizing agent, that is, respiratory oxygen made available through the reduction of the nitrate ion.

The difference between the CO_2 evolution for corresponding cultures of the plus-N and the minus-N cultures was calculated for each oxygen tension and was plotted against oxygen levels to form the broken-line curve of figure 1. This calculation gives the value of that portion of the CO_2 output which is associated with the utilization of a supply of nitrate ions. It is hereafter termed "extra CO_2 ."

The rate of production of extra CO_2 (as shown in figure 1) is highest at the lowest oxygen tension in the substrates and represents an anaerobic phase of respiration. When this evolution of extra CO_2 is considered in the light of the influence of the oxygen tension upon the nitrate absorption of these plants, as shown in the lower graph of figure 1, the significance of the relationship between extra CO_2 output and oxygen tension becomes apparent. The maximum rate of extra CO_2 production, found at zero oxygen, is directly correlated with both the nitrate absorption and nitrate reduction rates, which are also found to be maximum under these anaerobic conditions. After 23 days of oxygen treatment at the four oxygen levels, the rate of nitrate absorption in the plus-N cultures is highest under anaerobic conditions. Analyses of the roots, however, show relatively little nitrogen present as nitrate in anaerobically treated roots compared to those grown with an adequate oxygen supply. It is therefore evident that in the soybean roots the nitrate ions are much more rapidly reduced under anaerobic conditions than under the aerobic conditions attained with an adequate oxygen supply. Thus the high yield of extra CO_2 by the soybean roots of the plus-N cultures under anaerobic conditions must be ascribed to the abnormally high rate of nitrate reduction under these conditions of oxygen starvation.

The effects of aeration treatment upon the respiration of the roots of oat plants were compared to those previously obtained with soybeans. The technique used with these plants was the same as that employed with soybeans, but the minus-N to plus-N treatment was omitted. The nitrogen treatments and the four oxygen treatments were initiated simultaneously and continued for a period of 10 days. The rates of nitrate absorption and carbon dioxide production were measured over the 24-hour interval terminating the 10 days of the treatment period at the different oxygen levels. The data were calculated in terms of a unit weight of 10 gm. of fresh root tissue and a time interval of 24 hours. The extra CO_2 production was calculated as before and represents the difference between the rate of respiration of the plus-N and minus-N plants at each oxygen level. The values were plotted against oxygen levels and are given in the broken-line curve

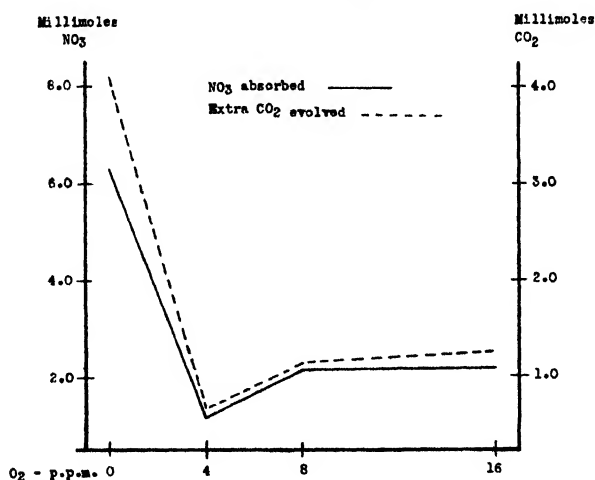


FIG. 1. RELATION BETWEEN RATES OF NITRATE-ION ABSORPTION AND EXTRA CO_2 PRODUCTION BY SOYBEAN ROOTS AFTER 23 DAYS OF TREATMENT AT FOUR OXYGEN LEVELS

of figure 2. The rates of nitrate absorption for the plus-N plants were plotted against the oxygen levels and are presented in the upper graph of figure 2.

The correlation between the two curves is good even though the oxygen treatments were conducted for only 10 days. It is to be noted that the nitrate absorption rates for the oat plants as for soybeans are maximum at 0 p.p.m. of oxygen. That the extra CO_2 rate is likewise maximum at zero oxygen tension is of much importance in illustrating the close relationship between extra CO_2 production and nitrate reduction, which is also maximum at zero oxygen, as indicated by Shive (9, 12) and others. Such a correlation is found, however, only when the rate of nitrate absorption has been accelerated under the influence of anaerobic conditions or at low oxygen tensions as a result of the development of metabolic systems capable of a high efficiency in nitrate reduction under such conditions. It is only after the plants have readjusted themselves to the conditions of oxygen deficiency and a steady state is attained in the rate of nitrate

absorption that the latter may be regarded as an approximate index of the rate of nitrate-ion reduction (assimilation). Though the rate of extra CO_2 production is shown to be associated with both nitrate absorption and nitrate reduction, it is the latter process which is primarily responsible for this yield of anaerobic or extra CO_2 . This is emphasized by the fact that no correlation was found between the CO_2 output and the nitrate intake during the first 24-hour experimental interval immediately following the transfer of the plants from the adequately aerated solutions in which the plants had been grown to those at the various oxygen levels at the beginning of the 10-day treatment period. The major factor responsible for the production of the extra CO_2 is this rate of nitrate reduction and not that of nitrate absorption.

Experiments with tomato plants conducted in the same way as were those with oat and with soybean plants show that the rate of nitrate-ion absorption

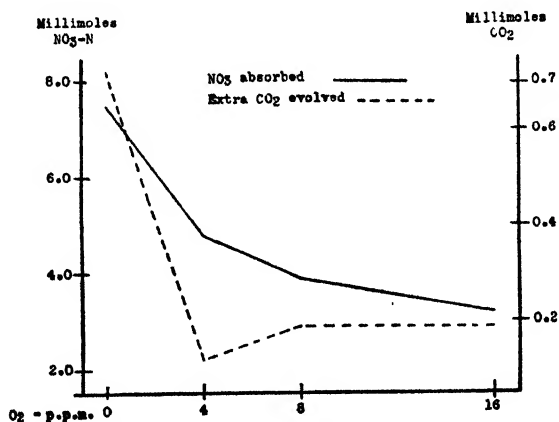


FIG. 2. RELATION BETWEEN RATES OF NITRATE-ION ABSORPTION AND EXTRA CO_2 PRODUCTION BY THE ROOTS OF OAT PLANTS AFTER 10 DAYS OF TREATMENT AT FOUR OXYGEN LEVELS

of tomato roots is influenced by the oxygen tension in a manner similar to that of the oat roots. The data for nitrate absorption by tomato roots after 1 week of treatment at the different oxygen levels follow curves similar to those of figures 1 and 2.

DISCUSSION

When plants are transferred from liquid substrates in which the oxygen tension is in equilibrium with air to substrates at different levels of dissolved oxygen, the absorption of nitrates by roots at first appears to follow the general course of absorption of other ions—the absorption rate being in direct relation to the oxygen tension up to the point where oxygen is no longer a limiting factor for the metabolic processes associated with ion absorption. This general relationship between ion absorption and oxygen tension of the nutrient substrate has been so strongly supported by the work of Hoagland and Broyer (6), Steward *et al.* (13), Burström (2), and Lundegårdh and Burström (7) that it appears to have re-

ceived sufficient experimental confirmation to establish it as a general principle for the absorption and accumulation of ions.

After continued exposure of the roots to low oxygen tension a steady state is gradually attained in which the relationship between oxygen tension and nitrate-ion absorption is radically altered from the initial state. The result is a shift in the absorption maximum from the aerobic to the anaerobic condition. This change occurs more rapidly with oat roots than with soybean. The tomato also responds more rapidly than the soybean to low oxygen conditions.

The high rate of nitrate assimilation under anaerobic conditions evidently promotes the absorption of that ion. The atomic oxygen of the nitrate ion may be an important factor in the assimilation of the nitrate ion, since under anaerobic conditions high nitrate-reducing power of the tissues favors the utilization of this source of oxygen in the respiratory processes of the roots cells. Such a condition has been suggested by Arnon (1).

It is certain that respiration of sugar is associated in some manner with the process of nitrate assimilation. Unpublished data on the carbohydrate analyses of the soybean and oat plants used in these experiments show that, as usual (8), in the absence of a nitrate supply to the roots, there is an accumulation of carbohydrates, especially of the soluble-sugar fraction, in the plants. This indicates that in the plus-N plant the carbohydrates are utilized in nitrate reduction and accumulate when the plants are given a deficient nitrate supply.

Thus it appears that there are at least two sources of the carbon dioxide measured in these experiments. First, CO_2 is produced by normal aerobic respiration in which the hexose substrate is completely broken down to CO_2 and H_2O . Since this is an aerobic process, it should theoretically be zero at zero oxygen tension and reach its maximum when oxygen is no longer the limiting factor for aerobic respiration. Second, the extra CO_2 produced from the partial oxidation of sugars in nitrate reduction has been shown by the data of figures 1 and 2 to be inversely related to the oxygen tension of the substrate. The total CO_2 output is the sum of both of these components plus a small amount of CO_2 from the anaerobic respiration at low oxygen tensions, the respiration of minus-N roots at the zero oxygen level. This agrees well with the respiration data obtained from soybean plants after 23 days of aeration treatment as given in figure 1, and for the oat plants, figure 2, which had received the various oxygen treatments for only 10 days.

From the data it is evident that the total CO_2 output of the root is the resultant of both the basic aerobic respiration and the anaerobic utilization of the oxygen made available by the reduction of the nitrate ion in the nitrogen assimilation process. As the major anion assimilation in plants is that of the nitrate ion, the reduction rate of this ion becomes important in any study of respiration based on CO_2 production.

SUMMARY

The rate of respiratory CO_2 produced by soybean, oat, and tomato roots grown in a basal nutrient solution adequately supplied with nitrate nitrogen (plus-N

cultures) was always higher than that of the roots of corresponding cultures grown without nitrogen (minus-N cultures).

The substitution of ammonium nitrogen for nitrate nitrogen in the nutrient substrate also produced lower yields of respiratory CO_2 than did corresponding cultures supplied with nitrate nitrogen, the values approaching those obtained with minus-N cultures.

The difference between the respiratory CO_2 produced by the plus-N roots and the minus-N roots (extra CO_2) is maximum at lowest oxygen levels and follows very closely the curves of nitrate-ion absorption and nitrate reduction as influenced by a wide range of oxygen levels in the nutrient substrate.

The production of the extra CO_2 appears to be directly associated with the evolution of oxygen in nitrate reduction and its utilization in the respiratory processes.

REFERENCES

- (1) ARNON, D. I. 1937 Ammonium and nitrate nitrogen nutrition of barley at different seasons in relation to hydrogen-ion concentration, manganese, copper, and oxygen supply. *Soil Sci.* 44: 91-121.
- (2) BURSTRÖM, H. 1939 Über die Schwermetallkatalyse der Nitratassimilation. *Planta* 29: 292-305.
- (3) GILBERT, S. G., AND SHIVE, J. W. 1941 A direct reading flowmeter and its use in respiration studies with plants. *Soil Sci.* 51: 55-58.
- (4) GILBERT, S. G., AND SHIVE, J. W. 1942 The significance of oxygen in nutrient substrates for plants: I. The oxygen requirement. *Soil Sci.* 53: 143-152.
- (5) HAMNER, K. C. 1936 Effects of nitrogen supply on rates of photosynthesis and respiration in plants. *Bot. Gaz.* 97: 744-764.
- (6) HOAGLAND, D. R., AND BROYER, T. C. 1936 General nature of the process of salt accumulation by roots with description of experimental methods. *Plant Physiol.* 11: 471-507.
- (7) LUNDEGÅRDH, H., AND BURSTRÖM, H. 1933 Untersuchungen über die Salzaufnahme der Pflanzen: III. *Biochem. Ztschr.* 261: 235-251.
- (8) NIGHTINGALE, G. T. 1937 The nitrogen nutrition of green plants. *Bot. Rev.* 3: 85-174.
- (9) PEPKOWITZ, L. P., GILBERT, S. G., AND SHIVE, J. W. 1944 The importance of oxygen in the nutrient substrate for plants—organic acids. *Soil Sci.* 58: 295-303.
- (10) PETERS, J. P., AND VAN SLYKE, D. D. 1932 Quantitative Clinical Chemistry. Vol. 2, Methods. Williams & Wilkins Co., Baltimore.
- (11) SHIVE, J. W., AND ROBBINS, W. R. 1940 Methods of growing plants in solution and sand culutres. N. J. Agr. Exp. Sta. Bul. 636.
- (12) SHIVE, J. W. 1941 The balance of ions and oxygen tension in nutrient substrates for plants. *Soil Sci.* 51: 445-459.
- (13) STEWARD, F. C., AND PRESTON, G. 1940 Metabolic processes of potato discs under conditions conducive to salt accumulation. *Plant Physiol.* 15: 23-61.
- (14) WARBURG, O., AND NEGELEIN, E. 1920 Über die Reduktion der Salpetersäure in grünen Zellen. *Biochem. Ztschr.* 110: 66-116.

VARIETAL SUSCEPTIBILITY IN GARDEN BEET TO BORON DEFICIENCY¹

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In studies already reported³ it was noted that certain varieties of garden beet differ in their response to boron deficiency. Good For All consistently showed a greater development of the root symptoms known as internal black spot than did Detroit Dark Red. Moreover, there were indications that a strain of the latter, designated as Morse's strain and herein referred to as Morse Detroit, was more susceptible than a standard strain of the variety which was designated as Ferry's strain. In the course of studies of other phases of boron deficiency, a survey was made of stocks of some of the more commonly used varieties of garden beet. This paper is a report of that study.

METHODS AND MATERIALS

Naturally boron-deficient soil in two locations in Wisconsin was used. The first location was near Winneconne where the soil was slightly alkaline Poygan silty clay loam. Trials were conducted here in 1940, 1941, and 1944. In 1941 a second location was selected near Clyman where the soil was slightly alkaline Clyde silt loam. Each lot of beet seed being tested was sown in a single-row plot in random order in each of four blocks. Each plot was at least 40 feet long. At the end of the season random root samples were taken from each plot. Each root was cut into quarter-inch slices, which were examined for internal black spot. The root was then placed in one of the following disease classes: no signs of disease, slight, moderate, severe. Giving each class equal weight, an index was calculated for each lot in the range of 0 representing no disease and 100 representing all roots severely diseased. In 1940, 50 roots per plot were examined; in 1941, 25 roots; in 1944, 100 roots. The data thus obtained were submitted to analysis of variance.

Lots of beet seed for the experiments were obtained from several commercial producers. It is not unexpected, therefore, that different lots within a variety were representative of different breeding lines. Those lots used in 1940 were repeated in 1941, but new stocks acquired for the 1944 trials, although from the same sources, were not necessarily identical with stocks previously used.

EXPERIMENTAL RESULTS

The indexes obtained in the trials of 1940 and 1941 are presented in table 1. Wide differences in susceptibility occurred. The most susceptible lots were

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³ Walker, J. C., J. P. Jolivet, and J. G. McLean. Boron deficiency in garden and sugar beet. *Jour. Agr. Res.* 66: 97-123. 1943.

Flat Egyptian, Light Red Crosby, Good For All, Morse Detroit, and one strain each of Early Wonder, Short Top Detroit, and Cannerns' Detroit. One strain of Early Blood Turnip had a low index in each trial, and Long Dark Blood was

TABLE 1

Internal black spot as shown by a disease index in strains and varieties of garden beet grown in boron-deficient soil near Winneconne and Clyman, Wis., 1940 and 1941

LOT NUMBER	VARIETY	WINNECONNE		CLYMAN 1941	Ave.
		1940	1941		
20	Flat Egyptian	72	76	53	67
16	Crosby Egyptian	48	46	42	45
21	Crosby Egyptian	31	44	18	31
19	Light Red Crosby	55	60	58	58
24	Asgrow Wonder	20	36	28	28
25	Asgrow Wonder	58	44	26	43
18	Tall Top Early Wonder	21	31	27	26
26	Early Wonder	63	69	35	56
29	Early Wonder	40	25	37	34
28	Early Wonder	35	42	22	33
38	Early Blood Turnip	48	47	32	42
35	Early Blood Turnip	28	34	18	27
34	Early Blood Turnip	4	13	3	7
2	Detroit Dark Red	43	40	32	38
9	Detroit Dark Red	30	41	25	32
5	Detroit Dark Red	25	43	29	32
4	Perfected Detroit	38	39	16	31
7	Perfected Detroit	35	38	18	30
6	Perfected Detroit	27	35	18	27
3	Morse Detroit	64	66	31	54
14	Cannerns' Detroit	61	58	44	54
15	Cannerns' Detroit	47	49	32	43
30	Good For All	75	61	41	59
10	Short Top Detroit	77	64	45	62
11	Short Top Detroit	58	29	43	43
23	Asgrow Canner	39	36	..	38
33	Ohio Canner	45	43	36	41
32	Ohio Canner	18	38	28	28
31	Ohio Canner	25	51	24	33
36	Long Dark Blood	1	..	0	0.5
Difference required for significance	19:1	17	14	16	
	99:1	23	18	22	

virtually free of disease. Other stocks were intermediate. There were, furthermore, some wide differences between stocks of the same variety. In Early Blood Turnip the index for lot 34 was significantly lower than that for lot 38 in each trial. In Early Wonder the index of lot 28 was significantly lower than that of lot 26 in two trials.

Detroit Dark Red variety was originally derived from Early Blood Turnip,

and from the Detroit, in turn, selections have led to the development of Perfected Detroit, Morse Detroit, Cannners' Detroit, Short Top Detroit, and Good For All. A comparison of these varieties leaves little doubt that through selection stocks have been developed which are more susceptible to internal black spot than the parent variety. Thus Good For All and one strain of Short Top Detroit were significantly more susceptible than the most susceptible strain of Detroit Dark Red in two of three trials. Morse Detroit was significantly more susceptible at the 5 per cent point than Detroit Dark Red in two trials.

Since the most severe tests were made at Winneconne, another trial was conducted in this location in 1944. A smaller number of varieties was selected and new lots of seed were obtained. The results of this test are given in table 2. Good For All, Flat Egyptian, and Morse Detroit were again the most suscep-

TABLE 2

Internal black spot in varieties of garden beet grown in boron-deficient soil near Winneconne, Wis., in 1944

VARIETY	DISEASE INDEX IN REPLICATES				MEAN DISEASE INDEX
	I	II	III	IV	
Flat Egyptian.....	63	79	59	73	69
Crosby Egyptian..	10	31	19	16	19
Early Blood Turnip	12	10	11	18	15
Detroit Dark Red	42	49	57	56	51
Perfected Detroit	54	61	42	63	55
Morse Detroit....	57	60	68	63	62
Good For All...	71	74	73	73	73
Asgrow Canner.....	27	33	35	44	35
Long Dark Blood	0	0	0	0	0
Difference required for significance (99:1).....					12

tible to boron deficiency, and the first two were significantly more so than the other six varieties tested. Detroit Dark Red, Perfected Detroit, and Asgrow Canner were again intermediate, and all were significantly more susceptible than Crosby Egyptian, Early Blood Turnip, and Long Dark Blood. Crosby Egyptian in this trial was distinctly less susceptible than either lot used in 1940 and 1941, and it and Early Blood Turnip were significantly more susceptible than Long Dark Blood in 1944.

SUMMARY AND CONCLUSIONS

Numerous observations are recorded in the literature of varietal differences in symptoms of mineral deficiencies. It is not surprising, therefore, to find this to be the case in garden beet in relation to boron deficiency. The wide differences which do occur in beet varieties are of major importance. It is not likely that any variety tested, aside from Long Dark Blood, can be relied upon to produce a healthy crop without correction of boron deficiency in the soil. It is

well to emphasize, moreover, that varieties, and strains within varieties, differ widely in susceptibility. This fact is of importance in comparing the results of soil treatments and in experimental work in this field generally. The demonstrated inherent nature of relative susceptibility to boron deficiency has a bearing of no mean significance upon beet improvement. Though it may not be wise to suggest the development of immune types, it is quite obvious that beet improvement without cognizance of susceptibility to boron deficiency may lead to disappointment. A case in point is that of Good For All, which was developed as a type especially useful in the packing of the fancy "rosebud" grade but which passed rapidly into the discard as a canning beet because of its extreme susceptibility to internal black spot in boron-deficient soils.

BORON CONTENT OF CITRUS TREES GROWN ON VARIOUS ROOTSTOCKS

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Although citrus rootstocks have long been known to affect the tree growth, disease resistance, compatibility, and fruit (8-12, 14, 16), surprisingly little is known regarding their effect upon absorption or solubility of nutrient or toxic elements. The earliest studies were those of Haas and Halma (3) who reported that the soluble magnesium as a percentage either of the dry matter or soluble ash in trunk bark is lowest in lemon and sour orange and highest in sweet orange and grapefruit. They also found that the values in the bark of the stock vary according to the scion variety with which it is combined. Though the basis of the reaction still is not understood, it was found by Halma and Haas (7) that the Almén test with minute samples of rootstock bark is a satisfactory means of distinguishing sour from sweet orange rootstocks in a mixed planting in the field. Later, Eaton and Blair (2), using reciprocally grafted sunflowers and Jerusalem artichokes in one series and lemons and Chinese box oranges in another, found that boron accumulations in the leaves of the scion were directly affected by the rootstocks upon which they were grown. Recently Roy (15) reported that leaves of citrus trees on sour orange rootstock contained considerably less boron than leaves of trees on other rootstocks, the leaves of trees on Rough lemon rootstock containing a relatively high boron content.

The results here presented deal largely with the rootstock variety as it affects the accumulation of boron in the fruit, leaves, and bark of citrus trees growing in experimental plots under closely comparable soil, cultural, and climatic conditions. In some cases differences were exposed by designating not only the rootstock variety, whether sweet or sour orange or grapefruit, but in addition also its source. The little that is known regarding the boron content of citrus flowers is included together with the manner in which these flowers grow. The conclusion is drawn from the leaf analyses that the significance of analytical data for boron may be increased by taking into full consideration the rootstock variety. Some notion regarding the mobility of boron is had from the studies on the water-solubility of boron.

METHODS

The samples were collected in such a manner as to make them comparable in most respects. Citrus flowers, fruits, and leaves were obtained from trees during a period in which there were no spray residues. Collections of the citrus flowers were not subjected to rain damage or zinc sprays. The fruit samples were washed and lightly brushed in running distilled water after the removal of the button and were wiped dry and peeled. A potato peeler was used to remove the outer or gland-bearing portion of the peel of some of the fruits.

Shallow wide glass dishes were used for drying the materials rapidly, especially the fruit pulp. Loss of juice resulting from tissue rupture in the pulp was entirely prevented by dividing the pulp into smaller portions as the drying progressed rather than at the start. The pulp, dried at 65° C., was ground in small lots at a time in a large mortar. Each citrus leaf was washed in running distilled water and wiped dry prior to being oven-dried. While the leaves were being washed individually, the experience itself suggested that the shape and consistency of the Valencia orange leaves seemed to vary somewhat according to the rootstock variety, though evaluation of the differences would be difficult. All plant materials were placed in a large well-ventilated oven at 65° C., and when dry they were ground in an electrically driven mill of suitable size. The bark samples were secured by thoroughly cleaning the trunk (scion and stock) with a steel brush followed by a bristle brush. Three long strips of bark, each one to several inches wide, were removed beginning below the first large branch and extending to just above the soil. The upper third of each of the three strips of the scion bark constituted the "upper third" sample of scion bark; the lower third of each of the three strips of scion bark constituted the "lower third" sample of scion bark. The three strips of bark below the bud union were designated as the rootstock bark. These bark samples were likewise dried at 65° C. and ground in a mill. After being finely ground the samples were placed in heavy brown folded paper envelopes which were slipped into paper bags upon which the data were written. These samples were stored in a well-ventilated oven below 50° C. until needed for sampling.

The first tests were for total boron. The accuracy of the methods (5, 6) for soil and plant materials in small samples, however, was such as to permit the fractionation of the boron into water-soluble and insoluble portions.

In order to collect the citrus flower samples at comparable stages of growth, frequent observations of their growth were made. A rubber stamp was used in printing India ink lines in various places on very young citrus flowers. The movement of the lines was then used as an indicator of growth.

FLOWERS

The growth of hundreds of lemon and orange flowers was followed by many observations and recordings. These showed that the principal growth in citrus flowers (fig. 1) is made near the base of the petals (corolla), where it is somewhat hidden by the green sepals. Growth in the flower therefore occurs largely in a protected region that likewise protects certain pests. The point of interest is that the basal growth in the flowers of citrus, a dicot, is of the same type as that in the fruits of the date palm (4), a monocot.

The lemon flowers of sample 2 in table 1 were small and weak, gum exudations occurring where flower abscissions had taken place (6). When boron was lacking in the culture solution, the lemon flowers (sample 2) contained less boron than when boron was adequate in the solution (sample 1), both boron fractions showing the effect of the boron deficiency. In both samples 1 and 2 the water-soluble boron was less than the water-insoluble boron.

The data for the fully open flowers (samples 3 to 7 inclusive) show the uniformity in the water-insoluble boron and the relatively low water-soluble boron in the lemon and grapefruit flowers as compared with that in orange flowers.

In samples 8 to 9 the flowers were not quite open, whereas in samples 10 to 18 inclusive the flowers were fully open. In fully open flowers the fluctuations in boron content occur in the soluble-boron fraction. The values for soluble boron in samples 11 and 12, where cover crops alone were used, were lower than where

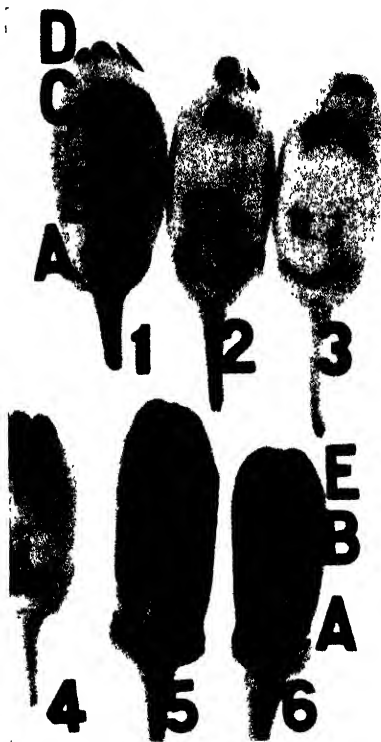


FIG. 1 GROWTH OF ORANGE AND LEMON FLOWERS

1-4, orange; 5 and 6, lemon. A, India ink lines stamped across tips of sepals and base of petals of young flowers. Growth has resulted in the movement of the marking from A to B. Other lines C, D, and E made across the flower tips indicated little if any growth near the tip.

none were grown, possibly suggesting that the cover crops were using some of the boron that otherwise would have been absorbed by the tree. Manure treatment (sample 13) of the soil was accompanied by a reduced soluble-boron content in the flowers. The microorganisms involved in the decomposition of the organic matter may have utilized much of the soluble boron. The soluble boron in the flowers of orange trees (samples 10 to 18 inclusive) exceeded the insoluble boron, whereas in the lemon and grapefruit flowers (samples 3, 4, 5, 8, and 9) the soluble was much lower than the insoluble boron. This condition may be

TABLE 1
Boron content of citrus flowers

SAMPLE NUM- BER*	SCION VARIETY	ROOTSTOCK VARIETY	LOCATION	TREATMENT	BORON IN DRY MATTER		
					Water- soluble	Water- insoluble	Total
1	Eureka lemon	Sweet orange	Culture solution	pH 4.5; 0.1 p.p.m. boron	p.p.m. 16.71	p.p.m. 19.63	p.p.m. 36.34
2	Eureka lemon	Sweet orange	Culture solution	pH 4.5; no boron	10.64	13.93	24.57
3	Eureka lemon		Citrus Experi- ment Station, pathology plots	Manure and cover crop	6.70	16.85	23.55
4	Lisbon lemon				10.30	17.40	27.70
5	Grape- fruit				7.00	15.80	22.80
6	Valen- cia or- ange				20.15	16.55	36.70
7	Navel orange				14.98	16.35	31.33
8	Eureka lemon	Sour or- ange	{ Citrus Experi- ment Station, Field 3	Manure; inorganic ni- trogen; cover crop	11.18	32.50	43.68
9	Eureka lemon	Sour or- ange			9.85	23.39	33.24
10	Wash- ington navel orange	Sweet orange	Citrus Experi- ment Station, fertilizer plots	Plot L14; none	25.25	15.15	40.40
11				Plot D12; cover crop	18.55	16.60	35.15
12				Plot J4; cover crop	16.55	15.65	32.20
13				Plot D20; manure equal to 3 pounds N in fall; cover crop	16.50	14.23	30.73
14				Plot D32; $\text{Ca}(\text{NO}_3)_2$ equal to 3 pounds N; cover crop	20.45	16.57	37.02
15				Plot I6; urea equal to 3 pounds N; cover crop	21.58	15.65	37.23
16				Plot K14; NaNO_3 equal to 3 pounds N; cover crop	21.98	17.24	39.22
17				Plot D46; $(\text{NH}_4)_2\text{SO}_4$ equal to 3 pounds N; cover crop	22.50	17.30	39.80
18				Plot D42; $\text{Ca}(\text{NO}_3)_2$ equal to 5 pounds N; cover crop	24.65	16.17	40.82

* Dates of collection: 1 and 2, November 29, 1938; 3-7 incl., May 1, 1935; 8 and 9, April 25, 1929; 10-18 incl., April 13, 1942.

related to the more vigorous growth of lemon and grapefruit trees over that of orange trees.

FRUIT

The fruits collected in the Citrus Experiment Station rootstock plots were average in size. A sufficient number of small fruits were found in one case to allow a test of the effect of size on boron content.

As shown in table 2, the concentration of boron was greater in the peel of Valencia oranges than in the pulp. A higher concentration of boron was found in the sample in which the fruits were very small (sample 2) than in the sample in which the fruits were of average size (sample 5). The boron content of the peel of Valencia oranges from trees on sweet and sour rootstocks was slightly less than when other rootstocks were used.

TABLE 2

Boron content of peel and pulp of Valencia oranges collected May 25, 1944 from trees on various rootstocks

SAMPLE NUMBER	ROOTSTOCK VARIETY	LOCATION OF TREES IN CITRUS EXP. STA. ROOTSTOCK PLOTS	BORON IN DRY MATTER	
			Peel	Pulp
			p.p.m.	p.p.m.
1	Siamese grapefruit	S1, A, R32, T1-5	27.06	15.30
2	Duncan grapefruit*	S1, A, R31, T1-5	25.19	15.15
3	Trifoliolate orange	S1, A, R21, T1-5	24.88	13.00
4	Rough lemon	S1, A, R30, T1-5	22.00	13.65
5	Duncan grapefruit	S1, A, R34, T11-15	21.88	11.70
6	Same as scion†	S1, A, R18, T6-10	21.88	13.50
7	C. E. S. 362 sweet orange	S1, A, R36, T1-5	21.48	13.00
8	Brazilian sour orange	S1, A, R29, T1-5	20.75	7.60
9	Koethen sweet orange	S1, A, R35, T1-5	19.19	10.35
10	African sour orange	S1, A, R27, T1-5	19.06	13.75

* Fruit very small.

† Rooted cutting from East Highland.

Samples of Valencia oranges each consisting of 25 fruits were collected May 26, 1944, from the Citrus Experiment Station Pathology Division plots at Riverside. On sweet orange rootstock (R20, T6, 8, 9, 10) the boron in the dry matter of the peel of Valencia oranges was 23.25 p.p.m. and in the dry pulp 13.75 p.p.m. On sour orange rootstock (R20, T17-20) the values were 22.56 and 11.90 p.p.m. respectively. The closeness of the values for the fruits of trees on these two rootstocks is in agreement with the data given in table 2.

Little if any change occurs in the boron content in the peel of Lisbon lemon fruits during natural coloring while attached to the tree. On November 26, 1942, samples of fruits of Lisbon lemon were collected in the Citrus Experiment Station rootstock plots at Riverside. The dry matter of the peel of green fruits contained 16.50 p.p.m. boron, and that of tree-ripe fruits from the same tree 16.25 p.p.m.

Gradients occur in the boron content of the peel of Valencia orange and Eureka

lemon fruits. The outer peel was removed to a depth just below the oil glands and was dried separately. Table 3 shows that the boron content of the outer peel of oranges and lemons differs from that of the inner peel and the differences are greatest when the rootstock is sour orange.

TABLE 3
*Boron gradient in the peel of Valencia orange and of Eureka lemon fruits**

SCION VARIETY	ROOTSTOCK VARIETY	LOCATION OF TREES IN CITRUS EXP. STA. ROOTSTOCK PLOTS	BORON IN DRY MATTER		
			Outer peel	Inner peel	Difference
			<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Valencia orange	Sweet orange	Path. R20, T6, 8, 9, 10	27.80	29.20	1.40
Valencia orange	Sour orange	Path. R20, T17-20	20.35	25.60	5.25
Valencia orange	Koethen sweet orange	S1, A, R28, T6-10	28.40	25.60	-2.80
Valencia orange	Standard sour orange	S1, A, R23, T11-15	19.10	27.40	8.30
Eureka lemon	Bessie sweet orange	B, R27, T6-10	18.50	17.60	-0.90
Eureka lemon	Rough lemon	B, R26, T1-5	15.90	21.30	5.40
Eureka lemon	African sour orange	B, R40, T6-10	10.95	23.25	12.30

* Fruits collected July 17, 1944; Valencia orange fruits fully mature; lemon fruits at silver stage of coloring on the tree.

LEAVES

The determinations of the boron content of citrus leaves were completed before the report (15) for citrus leaves in Florida was available. The data for the two citrus areas appear to be in substantial agreement. In table 4 are given the locations of the Valencia orange trees in the rootstock trials at Riverside and the water-soluble and water-insoluble boron concentrations in the dry matter of the leaves. Total boron was also determined, and the values agreed closely with the sums of the values of the water-soluble and water-insoluble fractions.

In table 4 the values for the water-insoluble boron are remarkably uniform, regardless of the rootstock variety. The variations that occur in the total boron content of Valencia orange leaves from trees on various rootstocks are due primarily to the differences in the water-soluble boron content.

The immobility of boron in citrus leaves has been stressed considerably (2, 15). It was shown (6) that citrus leaves can withstand a lack of boron in a culture solution much better when fruits are attached to the shoots than when the shoots are devoid of fruit.

Valencia orange leaves from trees on shaddock root vary greatly in their boron content, depending on the kind of shaddock, as for example, the lemon or the Siamese type (table 4). Likewise, not all grapefruit rootstocks behave alike, as seen in the data for Duncan and C. E. S. 343.

These data indicate the unreliability of collecting leaf samples without due regard to the rootstock variety. The rootstock variety in many citrus orchards

TABLE 4

Rootstock variety as related to the boron content of mature Valencia orange leaves

ROOTSTOCK VARIETY	LOCATION IN ORCHARD (C.E.S. Field S1)			BORON IN DRY MATTER		
	Block	Row	Trees	Water-soluble	Water-insoluble	Total
				<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Trifoliolate orange	C	20	1-5	101.75	17.50	119.25
	A	27	11-15	97.94	15.85	113.79
	A	21	1-5	105.88	11.66	117.54
	B	18	11-15	120.03	12.28	132.31
	A	22	6-10	103.00	12.60	115.60
				105.72	13.98	119.70*
Lemon shaddock	A	33	11-13	72.13	12.91	85.04
Rough lemon	A	32	6-10	65.19	11.32	76.51
	A	30	1-5	57.82	16.57	74.39
				61.61	13.95	75.45
Savage citrange	A	23	6-10	64.26	15.44	79.70
	A	22	1, 2, 4, 5	57.13	13.78	70.91
				60.70	14.61	75.31
Cleopatra mandarin	A	32	11-15	60.00	15.13	75.13
	A	31	11-15	60.57	17.69	78.26
				60.29	16.41	76.70
Sampson tangelo	A	31	6-10	51.69	16.06	67.75
	A	30	6-10	55.63	18.82	74.45
				53.66	17.44	71.10
Siamese shaddock	A	32	1-5	46.44	11.81	58.25
	A	35	11-15	49.76	14.79	64.55
				48.10	13.30	61.40
Duncan grapefruit	A	34	11-15	46.25	17.47	63.72
	A	31	1-5	47.57	15.85	63.42
				46.91	16.66	63.57
C. E. S. 362 sweet orange	A	29	6-10	48.88	18.13	67.01
	A	36	1-5	40.38	14.54	54.92
				44.63	16.34	60.97
Koethen sweet orange	A	35	1-5	37.00	16.22	53.22
	A	28	6-10	46.76	16.04	62.80
				41.88	16.13	58.01
C. E. S. 343 grapefruit	A	33	1-5	40.19	13.13	53.32
	A	36	11-15	38.69	15.94	54.63
				39.44	14.54	53.98

TABLE 4—Continued

ROOTSTOCK VARIETY	LOCATION IN ORCHARD (C.E.S. Field 51)			BORON IN DRY MATTER		
	Block	Row	Trees	Water-soluble	Water-insoluble	Total
Rubidoux sour orange				<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
	A	33	6-10	37.69	16.94	54.63
	A	28	1-5	27.50	14.60	42.10
African sour orange				32.60	15.77	48.37
	A	30	11-15	32.82	14.54	47.36
	A	27	1-5	27.25	13.00	40.25
Brazilian sour orange				30.04	13.77	43.81
	A	29	11-15	24.07	14.44	38.51
	A	29	1-5	34.13	14.13	48.26
				29.10	14.29	43.39

* Average values are in boldface type.

is partly or totally unknown. Thus it is difficult to know whether the results of Kelley and Brown (13), which show that the boron content of the normal leaf varies from only a few parts per million to approximately 100 p.p.m., represent variations due to differences in boron content in the soils of the orchards or differences in boron absorption as a result of the various rootstock varieties. Leaf analysis (1) thus becomes a more useful aid in the nutrition of citrus when more factors such as the rootstock variety are known.

Samples of citrus leaves were collected from trees on several varieties of citrus rootstocks in the Rubidoux plots in 1925 and 1928. The data for the boron content of the leaves are given in table 5. When Valencia orange or Eureka lemon was the scion, the leaves contained the least boron when sour orange was the rootstock. The relative order of the rootstocks is in agreement with the results given in table 4. For a given location the water-insoluble boron is fairly uniform.

It is of interest in table 5 that in two trees in which sour orange was budded on Eureka lemon and the sour orange in one case was rebudded to Eureka lemon so as to cause a sour orange sandwich, the boron contents of the Eureka lemon and of the sour orange leaves were low and very nearly the same.

The dry matter in the leaves of seedling orange trees of the rootstock varieties grown in the Citrus Experiment Station Pathology Division plots was tested for boron, and the highest concentration was found in the leaves of Trifoliate orange (table 6). Sour orange leaves tended to be slightly lower in boron content than sweet orange leaves. Differences in boron content of sweet and sour orange seedling leaves were evident even in very small nursery plants. The results in tables 4, 5, and 6 show the desirability of knowing not only the variety but also the source of the rootstock.

Table 7 shows the low boron content of lemon leaves when sour orange is the rootstock. Grapefruit and lemon leaves showed markedly lower boron when

the rootstock is sour orange than when it is sweet orange. The boron differences resulting from the rootstock effect in navel orange leaves were relatively small in comparison with those found in grapefruit and lemon leaves, sweet orange giving slightly greater values than sour orange. Thus the rootstock effect of sweet and

TABLE 5

Effect of the rootstock variety on the boron content of mature leaves of the scion

SCION VARIETY	ROOTSTOCK VARIETY	DATE OF COLLECTION	LOCATION	BORON IN DRY MATTER OF LEAVES		TOTAL BORON IN DRY MATTER OF LEAVES	
				Water-soluble	Water-insoluble	Calculated	Determined
				p.p.m.	p.p.m.	p.p.m.	p.p.m.
Valencia orange	Trifoliolate orange	Dec. 16, 1925	Rubidoux, R3	126.27	18.50	144.77	149.17
Valencia orange	Sweet orange	Dec. 16, 1925	Rubidoux, R6	85.00	16.60	101.60	104.17
Valencia orange	Pomelo	Dec. 16, 1925	Rubidoux, R4	75.23	16.63	91.86	100.00
Valencia orange	Sour orange	Dec. 16, 1925	Rubidoux, R5	66.07	16.03	82.10	83.92
Valencia orange	Sweet orange	Feb. 16, 1928	Rubidoux, Plot U, T25	132.13	21.94	154.07	144.00
Valencia orange	Pomelo	Feb. 16, 1928	Rubidoux, Plot U, T35	83.92	21.25	105.17	104.34
Valencia orange	Sour orange	Feb. 16, 1928	Rubidoux, Plot U, T30	73.20	20.30	93.50	...
Eureka lemon	Sweet orange	Feb. 16, 1928	Rubidoux, Plot U, T5	81.55	18.56	100.11	99.40
Eureka lemon	Pomelo	Feb. 16, 1928	Rubidoux, Plot U, T4	71.00	15.70	86.70	87.50
Eureka lemon	Sour orange	Feb. 16, 1928	Rubidoux, Plot U, T10	53.06	15.85	68.91	67.33
Mexican lime	Eureka lemon	June 3, 1928	Pasadena	154.38	10.63	165.01	
Eureka lemon*		June 26, 1943	C. E. S. Path. R18T21-24	47.80	15.50	63.30	
Sour orange		June 26, 1943	C. E. S. Path. R19T21-24	42.00	18.25	60.25	

* Sour orange sandwich.

sour orange on the boron content of navel orange leaves resembles more nearly that found in Valencia orange leaves (table 4).

Table 7 also shows the relatively uniform water-soluble boron content with the sour orange rootstock on both dates of collection, whereas with sweet orange rootstock the content varied with the time of collection.

The data in table 8 give some idea of the boron content of the sap and of the

dry matter of citrus leaves from budded trees without consideration of the rootstock. The values for the boron content when determined in the dry matter are much higher than when determined in the extracted leaf sap.

Table 6 is of key importance in fully understanding tables 4, 5, and 7. Table 6 shows the boron content of the leaves of large seedling citrus trees in relation to the seedling variety. Comparison of the data in tables 4-7 inclusive shows that the values for the boron content of the leaves of seedling trees occur in relatively the same order as those for the boron content of the leaves of whatever scion may be budded on these seedling varieties. In other words, the rootstock variety regulates the boron content of the leaves or impresses its own

TABLE 6
Boron content of mature leaves of seedling citrus trees

SAMPLE NUMBER	SEEDLING VARIETY	DATE OF COLLECTION	LOCATION AT CITRUS EXP. STA.	BORON IN DRY MATTER		
				Water-soluble	Water-insoluble	TOTAL
				p.p.m.	p.p.m.	p.p.m.
1	Trifoliate orange	June 26, 1943	Path. plots, R25, T9-13	74.90	16.37	91.27
2	Sweet orange	June 26, 1943	Path. plots, R31, T4, 8	32.40	16.28	48.68
3	Sour orange (Beladi) Tunis	June 26, 1943	Path. plots, R21, T21-23	31.90	13.07	44.97
4	Sour orange (Sicily)	June 26, 1943	Path. plots, R20, T23, 24	29.15	11.53	40.68
5	Sour orange	July 4, 1928	Path. plots	24.34	13.70	38.04
6	Koethen sweet orange, 1 foot high	June 26, 1943	Nursery adjoining Path. plots	58.07	17.13	75.20
7	Brazilian sour orange, 1 foot high	June 26, 1943		39.13	10.88	50.01

type of boron absorption or accumulation on leaves, regardless of whether these are a part of the budded scion or a part of the original seedling. The nature of the cells that constitute the root tissues of the various citrus varieties is largely responsible for the differences in boron absorption of the various rootstocks. Leaves of young seedling nursery trees (table 6) in which the roots are relatively close to the surface show the same order of boron content in relation to the variety as when the trees are much older and the roots are fully developed at their accustomed soil depths.

Emphasis should also be placed on the relative uniformity of the content of water-insoluble boron for the various parts of any variety of scion regardless of the rootstock. The large amounts of water-soluble boron found with certain rootstock varieties are excesses beyond the needs of the plant (luxury consump-

TABLE 7

Effect of sweet and sour orange rootstocks on the boron content of mature healthy leaves of grapefruit, lemon, and navel orange trees

SCION ROOTSTOCK	DATE OF COLLECTION*	LOCATION IN THE PATH. PLOT AT CITRUS EXP. STA.		BORON IN DRY MATTER		
		Row	Tree	Water- soluble	Water- insoluble	Total
Marsh grapefruit	Oct. 3	18	2	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Sweet orange				56.50	14.37	70.87
Marsh grapefruit	Oct. 3	18	6	30.00	14.42	44.42
Sour orange						
Marsh grapefruit	Dec. 11	18	3	66.80	10.13	76.93
Sweet orange	Dec. 11	18	7	29.30	8.03	37.33
Marsh grapefruit						
Sour orange						
Eureka lemon	Oct. 3	30	6	91.44	16.50	107.94
Sweet orange	Oct. 3	30	2	41.40	14.38	55.78
Eureka lemon						
Sour orange	Dec. 11	30	7	72.47	14.70	87.17
Eureka lemon						
Sweet orange	Dec. 11	30	3	41.10	13.48	54.58
Eureka lemon						
Sour orange	Oct. 3	13	1, 2	48.30	16.12	64.42
Navel orange						
Sweet orange	Oct. 3	6	1, 2, 4	42.50	14.60	57.10
Navel orange						
Sour orange	Dec. 11	13	3, 4
Navel orange						
Sweet orange	Dec. 11	6	5, 6, 7
Navel orange						
Sour orange						

* All collections made in 1930.

TABLE 8

Boron in the dry matter and expressed sap of mature citrus leaves

LEAVES*	BORON IN EXPRESSED LEAF SAP	BORON IN DRY MATTER OF LEAVES		
		Water-soluble	Water-insoluble	Total
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Navel orange	66.15	81.83	14.62	96.45
Eureka lemon	53.52	75.30	11.05	86.35
Marsh grapefruit	30.77	46.30	13.98	60.28

* Collected April 5, 1943, in the Path. plots at the Citrus Exp. Sta., Riverside.

tion). There is no reason to assume that the differences among the rootstock effects on mineral nutrition are confined solely to boron.

BARK

Boron in the dry matter of citrus trunk bark (table 9) appears to be largely water-insoluble. Bark samples were collected with respect to the scion and rootstock varieties, the sampling date, and the location of the bark samples on the scion trunk. The data for the boron content of these bark samples are given in table 10.

With lemon scions there was more water-soluble boron on both dates in the bark of the scion when sour orange rather than sweet orange was used as the rootstock. The dry matter of the bark of the sweet orange rootstock on both dates, however, contained slightly more water-soluble boron than that of the

TABLE 9
Boron in citrus trunk bark of the scion

SCION VARIETY	ROOTSTOCK VARIETY	LOCATION	BORON IN DRY MATTER		
			Water-soluble	Water-insoluble	Total
			p.p.m.	p.p.m.	p.p.m.
Washington navel orange affected with scaly bark.....	Sour orange	Arlington	5.00	24.75	29.75
			3.65	18.68	22.33
Sampson tangelo	Sour orange	C. E. S. R17T1	5.27	17.79	23.06
Savage citrange*	C. E. S. R17T41	3.82	27.10	30.92
Trifoliate orange*	Seedling	Rubidoux plots	5.24	17.40	22.64
Marmumi kumquat*.....		8.60	22.45	31.05

* Samples collected by Dr. L. J. Klotz.

sour orange. Whether sweet or sour orange rootstock was used, there was a downward gradient in the concentration of water-soluble boron in the trunk bark. In the scion bark there was less water-soluble boron on December 11 than on October 3.

The total boron in the bark of lemon scions was greater than in that of grapefruit or orange scions. When grapefruit scions were used there was less soluble boron in December than in October in the bark of both the scion and rootstock. The bark of sour orange rootstock contained less soluble boron than that of sweet orange.

When navel orange scions were used, the water-soluble and total boron content in the scion bark was greater in December than in October. In December there was more water-soluble boron in sweet than in sour orange rootstock bark. The trunk bark of the scion and rootstock does not give so clear a picture of the boron situation within the tree as do the leaves. This probably is the result of the intermediate position of the trunk parts and their functions.

TABLE 10

Content and solubility of boron in the dry matter of the trunk bark of scion and rootstock in citrus trees as affected by the time of collection

DATE OF COLLEC- TION*	LOCATION IN C. E. S. PATH. PLOT		PORTION OF TRUNK BARK COLLECTED	VARIETY	BORON IN DRY MATTER OF BARK		
	Row	Tree			Water- soluble	Water- insolu- ble	Total
					p.p.m.	p.p.m.	p.p.m.
Oct. 3	30	6	Scion: upper third	Eureka lemon	21.20	29.10	50.30
			Scion: lower third	Eureka lemon	9.70	33.70	43.40
			Rootstock: to the first root	Sweet orange	5.74	19.75	25.49
	30	2	Scion: upper third	Eureka lemon	24.25	31.35	55.60
			Scion: lower third	Eureka lemon	12.95	32.85	45.80
			Rootstock: to the first root	Sour orange	4.90	21.55	26.45
Dec. 11	30	7	Scion: upper third	Eureka lemon	16.41	34.25	50.66
			Scion: lower third	Eureka lemon	8.55	34.40	42.95
			Rootstock: to the first root	Sweet orange	6.15	18.35	24.50
	30	3	Scion: upper third	Eureka lemon	18.65	28.70	47.35
			Scion: lower third	Eureka lemon	11.30	31.25	42.55
			Rootstock: to the first root	Sour orange	4.60	19.20	23.80
Oct. 3	18	2	Scion: upper third	Marsh grapefruit	4.93	23.05	27.98
			Scion: lower third	Marsh grapefruit	4.15	22.60	26.75
			Rootstock: to the first root	Sweet orange	8.00	19.88	27.88
	18	6	Scion: upper third	Marsh grapefruit	4.89	22.55	27.44
			Scion: lower third	Marsh grapefruit	3.54	26.83	30.37
			Rootstock: to the first root	Sour orange	4.93	20.34	25.27
Dec. 11	18	3	Scion: upper third	Marsh grapefruit	4.85	23.40	28.25
			Scion: lower third	Marsh grapefruit	5.80	18.45	24.25
			Rootstock: to the first root	Sweet orange	5.80	18.45	24.25
	18	7	Scion: upper third	Marsh grapefruit	4.00	22.45	26.45
			Scion: lower third	Marsh grapefruit	2.85	22.65	25.50
			Rootstock: to the first root	Sour orange	3.73	18.60	22.33
Oct. 3	13	1, 2	Scion: all	Navel orange	4.34	19.55	23.89
			Rootstock: to the first root	Sweet orange
	6	1, 2, 4	Scion: all	Navel orange	10.09	20.65	30.74
			Rootstock: to the first root	Sour orange
Dec. 11	13	3, 4	Scion: all	Navel orange	12.70	18.80	31.50
			Rootstock: to the first root	Sweet orange	13.65	19.55	33.20
	6	5, 6, 7	Scion: all	Navel orange	14.88	19.25	34.13
			Rootstock: to the first root	Sour orange	8.10	20.35	28.45
Dec. 11	4	6, 7, 8	Scion: upper third	Valencia orange	10.56	24.55	35.11
			Scion: lower third	Valencia orange	5.60	24.30	29.90
			Rootstock: to the first root	Sweet orange	7.70	18.60	26.30

* All collections made in 1930. Dr. L. J. Klotz assisted in the collecting of these samples.

SUMMARY

The investigation deals with the rootstock variety as it affects the accumulation of boron in the fruit, leaves, and bark of citrus trees growing in experimental plots under comparable soil, cultural, and climatic conditions. The source of the rootstock within a given rootstock variety may be reflected in some cases by differences in the boron accumulation in the leaves of the scion. The leaves of like scions vary in their boron content according to the rootstock variety. The variations in available boron at different soil depths, the transpiration rates, and the distribution of the roots in the soil may all be factors involved, but primarily it is the nature of the cells of the rootstock that accounts for the behavior in the scion accumulations.

The significance of analytical data for boron in healthy plants is enhanced by taking into consideration the rootstock variety and its source. The mobility of boron in citrus is far greater than is commonly understood.

The little that is known concerning boron in citrus flowers is discussed, as is also the method of growth of the flowers. The growth in citrus flowers (a dicot) is similar to that in the fruits of the date palm (a monocot). The boron content of citrus flowers was reduced when the boron supply was made inadequate. The water-insoluble boron content was uniform in the dry matter of citrus flowers. In the dry matter of lemon and grapefruit flowers, the water-soluble boron was low as compared with that in orange flowers.

The boron content of the peel of Valencia oranges from trees on sweet and sour rootstocks was slightly less than when other rootstocks were used. Gradients occur in the peel of Valencia orange and Eureka lemon fruits. Differences in the boron content of the outer and inner portions of the peel in orange and lemon fruits were greatest when the rootstock was sour orange.

The water-insoluble boron content of the dry matter of Valencia orange leaves of trees on various rootstocks is remarkably uniform. Large differences occur in the water-soluble and in the total boron content, and these differences are definitely related to the rootstock variety. This relationship is also shown for the leaves of lemon, grapefruit, and navel orange scions when grown on various rootstocks. The leaves of seedling trees of different varieties show roughly the same order of boron accumulation as do the leaves of other varieties used as scions on these same seedling roots. The effect of the rootstock on boron in scion leaves is slightly greater for sweet than for sour orange rootstocks, and the effects are greater for lemon and grapefruit than for the leaves of navel or Valencia orange scions.

The trunk bark does not give so clear a picture of the boron situation within the tree as do the leaves. This probably is the result of the intermediate position of the trunk parts and their functions.

REFERENCES

- (1) CHAPMAN, H. D., AND BROWN, S. M. 1943 Leaf analysis reveals needs, California experiments. *Citrus Leaves* 23: 9.
- (2) EATON, F. M., AND BLAIR, G. Y. 1935 Accumulation of boron by reciprocally grafted plants. *Plant Physiol.* 10: 411-424.

- (3) HAAS, A. R. C., AND HALMA, F. F. 1929 Chemical relationship between scion and stock in citrus. *Plant Physiol.* 4: 113-121.
- (4) HAAS, A. R. C., AND BLISS, D. E. 1935 Growth and composition of Deglet Noor dates in relation to water injury. *Hilgardia* 9: 295-344.
- (5) HAAS, A. R. C. 1944 The turmeric determination of water-soluble boron in soils of citrus orchards in California. *Soil Sci.* 58: 123-137.
- (6) HAAS, A. R. C. Boron in citrus trees. *Plant Physiol.* (In press).
- (7) HALMA, F. F., AND HAAS, A. R. C. 1929 Identification of certain species of citrus by colorimetric tests. *Plant Physiol.* 4: 265-268.
- (8) HALMA, F. F. 1943 Rootstock influence on the composition of Valencia orange fruit. *Amer. Soc. Hort. Sci. Proc.* 42: 349-352.
- (9) HODGSON, R. W., CAMERON, S. H., AND EGGERS, E. R. 1937 Rootstock and scion influence in citrus. *Calif. Citrogr.* 22: 110.
- (10) HODGSON, R. W., EGGERS, E. R., AND CAMERON, S. H. 1938 On the relation between vigor of scion variety and rootstock reaction in the lemon. *Calif. Citrogr.* 23: 290, 306.
- (11) HODGSON, R. W., AND EGGERS, E. R. 1938 Rootstock influence on the composition of citrus fruits. *Calif. Citrogr.* 23: 499, 531.
- (12) HODGSON, R. W., AND CAMERON, S. H. 1943 Some instances of scion dominance in citrus. *Amer. Soc. Hort. Sci. Proc.* 43: 131-138.
- (13) KELLEY, W. P., AND BROWN, S. M. 1928 Boron in the soils and irrigation waters of southern California and its relation to citrus and walnut culture. *Hilgardia* 3: 445-458.
- (14) RICHARDS, A. V. 1939 Influence of rootstocks on quality of citrus fruit. *Amer. Soc. Hort. Sci. Proc.* 36: 298.
- (15) ROY, W. R. 1943 Studies of boron deficiency in grapefruit. *Fla. State Hort. Soc. Proc.* 56: 38-43.
- (16) SINCLAIR, W. B., AND BARTHOLOMEW, E. T. 1944 Effects of rootstock and environment on the composition of oranges and grapefruit. *Hilgardia* 16: 125-176.

BOOKS

Colorimetric Determination of Traces of Metals. By E. B. SANDELL. Interscience Publishers, Inc., New York, 1944. Pp. 487, figs. 73. Price, \$7.

This is volume 3 of a series of monographs on analytical chemistry and its applications, published under the general title, "Chemical Analysis." The purpose of the author was to assemble the most modern methods in this field of analysis and to present them under one cover. The general divisions of the book include methods for the separation and isolation of traces of substances, colorimetry and spectrophotometry, and general colorimetric reagents. Specific methods are given for 45 elements and for the rare earths. Of particular interest to those engaged in soil and plant analysis are the instructions for Al, As, Ca, Co, Cu, Fe, Mg, Mn, Mo, Ni, K, Na, and Zn. This book should find a place in every laboratory where trace elements present an analytical problem.

The Future of Industrial Research. Standard Oil Development Company, New York, 1945. Pp. 173.

This book contains the papers presented at a meeting attended by some 500 chemists at the Waldorf-Astoria Hotel in New York City commemorating the silver anniversary of the Standard Oil Development Company. Addresses were given by Frank A. Howard, C. F. Kettering, Frank B. Jewett, Thomas Midgley, Jr., Harry L. Derby, Bradley Dewey, Warren K. Lewis, Edwin H. Land, Westbrook Steele, Earl P. Stevenson, Clyde E. Williams, A. C. Fieldner, and Robert P. Patterson. They present a varied and illuminating picture of concepts and philosophies of research, with particular reference to its application in the industrial field. Any student expecting to go into this type of research will find this volume of great interest and value, as will all those who aid in preparing students for this field of endeavor.

Good Soil. By S. GRAHAM BRADE-BIRKS. The English Universities Press Limited, London, 1944. Pp. 296, figs. 77. Price 3s.

This book is one of a series entitled "Teach Yourself Farming." The subject is approached "from the farmer's point of view," the purpose being to "give a general picture of the soil mantle, its properties, its origin, and its diversity." The intelligent farmer who has some knowledge of the sciences underlying that of the soil would find the material interesting and instructive. The approach to the subject is a modern one, and the presentation is to be commended. An interesting and new feature is found on the inside of the wrapper. It consists of a set of five test questions which the reader is invited to answer and send in for grading. The questions are: "Give an illustrated account of any one soil that you have studied and indicate how you would classify it. Give briefly the reasons for regarding every individual soil as a natural object. Describe a typical chernozem and under what circumstances would you expect to find such a soil? If you are thinking of acquiring a farm what observations would you make or cause to be made upon its soils? How far is national wealth to be estimated

in terms of good soil and what safeguards would you advise for the maintenance of the efficiency of the soil?"

A Manual of Soil Fungi. By JOSEPH C. GILMAN. The Collegiate Press, Inc., Ames, Iowa, 1945. Pp. 392, figs. 135. Price, \$5.

This is a very opportune time for the publication of a manual on soil fungi, now that so much interest has been aroused in their value as agents for the production of antibiotics. The purpose of the book is that of "placing a tool in the hands of investigators that will enable them to identify soil fungi which they may encounter in their work." The book contains a key to the classes, orders, and families of soil fungi, which are divided into the Phycomycetes, Ascomycetes, Fungi Imperfecti, and Mycelia Sterilia. The 135 figures constitute a highly important part of the presentation. No consideration is given to possible functions of the fungi, except in a very minor way in the introductory statement. The value of the book lies in its usefulness for reference purposes.

Microbial Antagonisms and Antibiotic Substances. By SELMAN A. WAKSMAN. Published by the Commonwealth Fund, 41 East 57th Street, New York, 1945. Pp. 350, figs. 34. Price, \$3.75.

The central theme of this book is that the soil is a natural medium for the development of antagonists that destroy pathogenic microorganisms, and a comprehensive review is presented of researches designed to test that concept. The results of the work in this field of endeavor have been so spectacular, the human values have already been so great, and the potentialities ahead are so important that all those who deal with the soil in any capacity will want to be informed on this subject. Those specifically engaged in this branch of microbiology will be delighted to find a bibliography of 1016 references. It may be well to add that, according to the author, "antagonism" is "the phenomenon of a living organism inhibiting the growth or interfering with the activities of another living organism as a result of the creation of unfavorable conditions in the medium or the production of a specific antimicrobial substance." Likewise, "antibiotic" means "inhibiting the growth or the metabolic activities of bacteria and other microorganisms by a chemical substance of microbial origin."

Two Billion Acre Farm. By ROBERT WEST HOWARD. Doubleday, Doran and Co., Inc., Garden City, New York, 1945. Pp. 209. Price, \$2.50.

In these days of paper shortage and the changes in format necessitated thereby, one often gets a great deal more value per page and volume than he did in the days before the war. This compact little volume is a case in point. It starts some 26,500 years ago with the fishermen from the Asiatic mainland who migrated to America, then follows the pioneers who hewed their way through the forests to conquer the plains, and ends with the modern farmer-cooperatives and their plans ahead. A great deal of reading and thought have gone into the preparation of this book, with its stories of men of action and the deeds they performed. To read it is to regain confidence in the future of our farmers.

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